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THE PHYSICOCHEMICAL INVESTIGATION OF SYSTEMS CONTAINING HALOGENIDES OF IODINE AND HALOGENIDES OF OTHER ELEMENTS.

VIII. ICl--KCl AND ICl--$AlCl_3$ SYSTEMS

Y. A. Fialkov and O. I. Shor

Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences

Little research has been done up to now on systems consisting of halogenides of iodine and halogenides of other elements, like the complex compounds formed in these systems, especially from the standpoint of physical chemistry.

Almost the only physicochemical research on systems of this sort has been the work done by Cornog and his associates [1] (measuring the vapor pressure and electrical conductivity of KCl – ICl and NH_4Cl – ICl systems, determining the solubility of KCl in ICl, and some other research) and the work done by our laboratory in investigating the electrical conductivity of systems consisting of ICl and IBr and one of these salts: KBr, KI, and $AlBr_3$ [2], the thermal analysis of the ICl – $AlBr_3$ and ICl – KI systems [3], and measurement of the viscosity of the IBr – $AlBr_3$ system [4].

Research on systems consisting of halogenides of the halogens and halogenides of other elements is of considerable importance for resolving a number of problems dealing with the chemistry of the polyhalogenides and related compounds.

In particular, the question of the nature of compounds of halogenides of iodine with halogenides of metals and nonmetals, as well as of their structure, remained unresolved until recently.

These compounds are usually classed as polyhalogenides, though there is reason to believe that many of them are double halogenides [4]. A conclusion of this sort may be reached, for example, from the results of an investigation of nitrobenzene solutions of ICl–KCl and ICl–$AlCl_3$ systems [5], as well as similar systems with bromides of iodine, potassium, and aluminum [6].

Investigation of these solutions by the method of ion transfer justified the assumption that the structure of ICl or IBr with KCl or KBr, respectively, is best expressed by the formulas $K[ICl_2]$ or $K[IBr_2]$; compounds of these same halogenides of iodine with $AlCl_3$ of $AlBr_3$ may be assigned the structure $I[AlCl_3]$ or $I[AlBr_3]$, which characterize these substances as double halogenides.

We resolved to investigate the systems ICl – KCl and ICl – $AlCl_3$ without any solvent present by the methods of thermal analysis, electrical conductivity, electrolysis, and ion transfer with a view to further study of the compounds of iodine halogenides with halogenides of potassium and aluminum and for confirmation of the conclusions reached as a result of our study of the nitrobenzene solutions mentioned above.

The preparation and refinement of the substances and the research methods have been described in our previous reports.

1. ICl – KCl System

The electrical conductivity of this system was measured by Cornog and Karges [1] at 35° throughout the range of 0.5 to 0.00993 mol. concentration. The values of electrical conductivity they obtained are plotted in Fig. 1.

Cornog and Bayer [1] determined the solubility of KCl and ICl in the 15-60° range and measured the vapor pressure of the KCl – ICl system at 25°; their results led them to the conclusion that there are two compounds – $KICl_2$ and KI_2Cl_3 (i.e., KCl·ICl and KCl·2ICl) – in this system. They obtained the second of these compounds from solutions of KCl and ICl by crystallization at temperatures below 45°. This compound is unstable, easily breaking down into $KICl_2$ and ICl.

To judge from the data cited by Cornog and Bayer, KCl is relatively insoluble in ICl; at 35°, for example, no more than 5.95 g of KCl dissolves in 100 g of ICl, corresponding to 11.5 mol. %; at 45° 13.2 mol.% of KCl is dissolved. Moreover, according to the data of the same authors, when equimolar mixtures of KCl and ICl are kept for a long time – a few weeks – the compound $KICl_2$ is formed.

We began our research with measurements of the electrical conductivity of the KCl – ICl system, bearing in mind that Cornog and Karges obtained their data only for relatively low KCl concentrations, up to about 2.5 mol.%.

We measured the electrical conductivity at 35° and 45°, adding weighed quantities of KCl to the iodine chloride in the vessel used to measure conductivity.

As KCl does not dissolve quickly in ICl when its concentration is high, the vessel was first kept in an air thermostat at 50-55° after a new portion of KCl was added and shaken periodically, after which the vessel was placed in a water thermostat and the electrical conductivity was measured. This operation was repeated several times until the electrical conductivity remained constant for each given concentration investigated.

The measured electrical conductivities are listed in Table 1 and in Fig. 1

As the concentration of KCl rises, the conductivity of the KCl – ICl system first rises: to 0.017-0.021 mhos at 6-8 mol.% of KCl. With a further increase in the KCl percentage, the system's conductivity begins to fall, finally remaining constant owing to the fact that under the experimental conditions no more KCl dissolves in the ICl.

The electrical conductivity of the ICl – KCl system is close to that of the nitrobenzene solutions of this system for identical concentrations of ICl and KCl, [9].

The temperature coefficient of conductivity is positive, rising with increasing concentration until about 8 mol. % of KCl, after which it is constant.

In Fig. 1 there are also plotted the values for specific conductivity

Table 1

Specific Conductivity of the KCl – ICl System

KCl (mol.%)	$x \cdot 10^3$ 35°	$x \cdot 10^3$ 45°
0.00	5.70	6.30
0.97	9.32	11.0
2.2	12.4	15.1
4.3	15.2	18.0
6.2	17.0	21.0
8.1	17.0	21.0
9.9	15.8	19.0
13.2	15.0	18.5
16.7	15.0	18.3

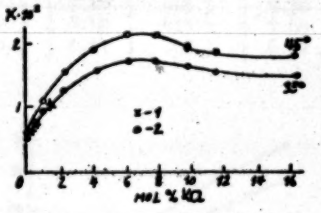

Fig. 1. Specific conductivity of the KCl – ICl system

1-Cornog and Karges data; 2-our data

of the ICl – KCl system obtained by Cornog and Karges [1]. At low KCl concentrations, these values coincide with those obtained by us.

It should be stated, however, that for purposes of comparison we used those Cornog and Karges figures that apply to the conductivity of the ICl-KCl system as a whole, although these authors, in an apparent endeavor to indicate the conductivity of KCl, deduct the conductivity of iodine chloride from the conductivity of the ICl-KCl system, forgetting the formation of co-ordination compounds of KCl and ICl in this system.

The values of specific gravity of the KCl – ICl system were measured at 35° and 45° up to 9 mol.% of KCl (Table 2, Fig. 2).

The specific gravity isotherms are straight lines.

The molecular conductivity of the KCl – ICl system was computed from the values of specific conductivity and specific gravity, in terms of KCl as the electrolyte (Table 3, Fig. 3).

With increasing dilution, the molecular conductivity increases. The variation of μ with dilution is "normal". Cornog and Karges made similar observations in the region of low KCl concentrations.

Thermal analysis. The limited and, what is more, extremely slow solubility of KCl in ICl makes it impossible to determine the temperature of crystallization

Table 2

Specific Gravity of the KCl – ICl System

KCl (mol.%)	$d_{20°}^{35°}$	$d_{20°}^{45°}$
0.00	3.199	3.169
0.89	3.192	3.168
1.76	3.190	3.166
2.85	3.188	3.168
3.90	3.179	3.157
5.16	3.176	3.154
5.55	3.173	3.150
5.84	3.171	3.146
7.99	3.168	3.144
8.96	3.160	3.135

Table 3

Molecular conductivity of the KCl – ICl system

KCl (mol.%)	35°		45°	
	φ	μ	φ	μ
0.97	5317	49.45	5365	59.02
2.2	2347	29.10	2368	35.75
4.3	1144	17.38	1153	20.76
6.2	797.1	13.65	803.5	16.87
8.1	590.5	10.04	595.0	12.50
9.9	486.0	7.68	489.3	9.30
11.6	142.3	6.19	415.1	7.89
13.2	364.6	5.47	367.1	6.72

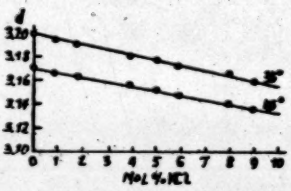

Fig. 2. Specific gravity of the KCl-ICl system.

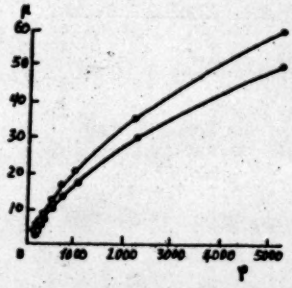

Fig. 3. Molecular conductivity of the KCl-ICl system

over a rather large concentration range, which is why we confined ourselves to measurements up to a concentration of 15.5 mol.% of KCl. In tests with KCl concentrations above 10 mol.% , the melts first had to be kept for a long time with frequent agitation.

The crystallization temperatures of the KCl – ICl system drop with increasing concentration of KCl, down to 12° at 11.8 mol.% of KCl (Table 4, Fig. 4). The crystallization temperature then starts to rise somewhat, but when the limit of KCl solubility is borne in mind, it is hard to ascertain the KCl concentration that corresponds to the eutectic point.

Electrolysis. Since the ICl – KCl system always contains a large excess of iodine chloride, in addition to the $KICl_2$ (or KI_2Cl_3 as well), because of the relatively low solubility of KCl in ICl, we had to bear in mind that the electrolysis of the co-ordination compounds would be accompanied by the electrolysis of the excess ICl.

Table 4

Thermal Analysis of the KCl–ICl System

KCl (mol.%)	Crystallization temperature	KCl (Mol.%)	Crystallization temp.
0.00	27.0°	8.73	13.0
0.91	25.5	8.79	13.0
1.01	24.5	10.3	12.5
2.88	22.0	11.84	12.0
3.04	21.5	15.6	13.0
5.15	16.0		

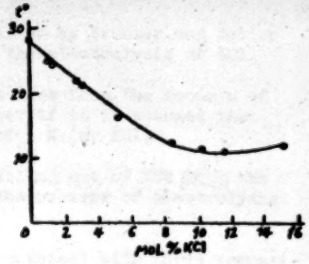

Fig. 4. Fusibility curve of the ICl–KCl system

In electrolyzing fused ICl, Brunner and Bekier, [7], observed the isolation of iodine at the cathode and chlorine at the anode.

This circumstance renders the quantitative investigation of the electrolysis of the ICl – KCl system quite difficult, and we therefore confined ourselves to the manifestations of the processes that occur during the electrolysis of this system.

We ran our electrolysis experiments in a U-shaped tube with platinum electrodes. A copper coulometer was connected into the circuit; the KCl concentration was 6.8-7.0 mol.%; the current ranged from 40 to 60 milliamperes at voltages of 8 to 14 volts. Electrolysis lasted 2.5 to 5.5 hours. After the run, the electrodes were washed with ether, dried, and weighed. The cathode gained weight in every run. The weight of the anode did not change. KCl was always found in the cathode deposit. In tests lasting 4-5 hours, crystalline iodine was also found deposited on the cathode.

The results of some of the tests are given in Table 5.

Table 5

Electrolysis of KCl-ICl System

KCl (Mol.%)	Current, milliamp.	Duration of test, hours	Copper deposited, g	Increase in cathode weight g	Cathode deposit
7.0	60	2:30	0.1517	0.1180	KCl
7.0	60	4:00	0.3005	0.2242	KCl
6.8	44	5:30	0.3864	0.2599	KCl and iodine

The deposition of KCl on the cathode is probably due to the fact that the metallic potassium deposited at the cathode reacts with the ICl during the electrolytic decomposition of the $KICl_2$, possibly in accordance with:

$$2K + ICl = KCl + KI;$$

$$KI + ICl = KCl + I_2.$$

Our experiments also confirmed the data published by Brunner and Bekier on the deposition of iodine at the cathode during the electrolysis of ICl.

The increase in weight of the cathode is much less than the amounts of KCl that might be computed from the deposited copper if it is assumed that the passage of 1 F corresponds to the deposition of 1 K (or KCl).

This is due to the partial dissolution or settling out of KCl from the cathode surface, as well as to the complexity of the process of electrolysis of the ICl – KCl system.

Investigation of ion transfer was effected in a vessel with three compartments, as described by V.A.Izbekov [8]. Platinum electrodes were used. The tests lasted 18 to 22 hours; the current used was 10-15 milliamp. In the tests 5.5-6 mol.% solutions of KCl in ICl were used.

The anode, cathode, and middle portions of the liquid were poured into flasks with ground-glass stoppers after each test, weighed, and analyzed as described in previous reports [5,6].

The results of these tests, listed in Table 6, show that chlorine migrates to the anode, and potassium and iodine to the cathode.

Table 6 -- see page 246 .

Turning to the quantitative results of these tests, we must bear in mind that ion transfer in the KCl – ICl system takes place as the result of the electrolysis of both the coordination compound formed in this system and of the excess ICl. We assumed that the transference number for K^+ in this system was the same as in the nitrobenzene solution of KCl – ICl where it was very close to 0.5 [9].

If it is assumed that the composition of this coordination compound is expressed by the formula $KICl_2$, there are x equivalents of iodine and $2x$ equivalents of chlorine transferred to the anolyte, for x equivalents of potassium transferred to the catholyte.

Let us assume that the electrolysis of y moles of ICl took place at the same time, which ought to result in the transfer of y equivalents of iodine to the catholyte and y equivalents of chlorine to the anolyte.

It follows that x equivalents of potassium and $y-x$ equivalents of iodine should be transferred to the catholyte, the anolyte receiving $y + 2x$ equivalents of chlorine.

According to the figures for Experiment 2, x = 0.0869:0.0391 = 2.2 milliequivalents; y = (0.2193:0.1269) + x = 3.9 milliequivalents.

The theoretical quantity of chlorine transferred to the anolyte ought to be 3.9 + 2·2.2 = 8.3 milliequivalents.

The actual transfer was 0.2248:0.0355 = 6.3 milliequivalents.

The same sort of computation for Experiment 3 gives the theoretical quantity of chlorine transferred to the anolyte ($y + 2x$) as 5.7 milliequivalents; the

experimental data yield 0.2736:0.0355 = 7.7 milliequivalents.

If the complexity of the system is borne in mind, possibly containing, in addition to ICl and KCl, KI_2Cl_3 and ICl_3 (which can be formed by the action of the chlorine liberated during electrolysis upon the ICl), as well as a certain conventionality about the transference number we assumed for K^+, we are justified in saying that the agreement of our experimental values with the theoretical is satisfactory as far as chlorine transference is concerned.

Thus, the experiments on the electrolysis and ion transfer in the ICl – KCl system confirm the formation of a coordination compound in this system, the most probable composition and structure of which is represented by $K[ICl_2]$.

2. ICl – $AlCl_3$ System

This system was first investigated by Fialkov and Kagan in a nitrobenzene solution [5,9]. Comparison of the results of conductivity measurements and cryoscopic investigation of the ICl – $AlCl_3$ – $C_6H_5NO_2$ led to the conclusion that $AlCl_3$ combines with iodine chloride to form a complex compound (apparently unstable). Study of the ion transfer showed that the iodine migrates to the cathode, whereas the aluminum in the complex anion moves to the anode.

As has already been stated, these facts made it necessary to investigate the ICl–$AlCl_3$ system with no organic solvent present.

Electrical conductivity of the ICl – $AlCl_3$ system. We measured the specific conductivity of this system at 35° and 45°. Using the ease with which this system can be supercooled, we succeeded in making measurements up to 54 mol.% of $AlCl_3$; at higher $AlCl_3$ percentages the system solidified at the measurement temperature.

The conductivity of the ICl-$AlCl_3$ system changes very peculiarly with changes in the concentration of $AlCl_3$: the conductivity drops slightly at first (up to 1.5 mol.% $AlCl_3$); then it increases, passing through a maximum at 10-13 mol.% of $AlCl_3$, after which it drops (Table 7 and Fig. 5).

Table 7

Specific Conductivity of the ICl – $AlCl_3$ System

$AlCl_3$ (Mol.%)	$\varkappa \cdot 10^3$		$AlCl_3$ (Mol.%)	$\varkappa \cdot 10^3$	
	35°	45°		35°	45°
0.00	5.51	5.61	13.22	7.53	9.62
0.81	5.13	5.37	19.65	5.98	8.03
1.42	4.73	5.21	24.77	4.71	6.48
1.79	5.18	5.75	30.80	3.89	5.37
2.41	5.57	6.52	36.66	3.56	5.03
5.89	6.70	8.61	45.04	3.20	4.48
7.28	7.09	9.15	49.08	3.13	4.28
9.44	7.78	9.79	53.71	3.11	4.10

It is worthy of note that the isotherms of electrical conductivity

follow a similar course in the ICl – $AlBr_3$ system [2].

The temperature coefficients of conductivity are positive, rising with increasing $AlCl_3$ concentrations up to 13 mol.%, after which they remain nearly constant.

The conductivity of the ICl-$AlCl_3$ system is many times higher that that of the ICl-$AlCl_3$-$C_6H_5NO_3$ system (at 18°) for identical ICl-$AlCl_3$ ratios.

The specific gravity of the ICl – $AlCl_3$ system was measured up to 29 mol.% of aluminum chloride at temperatures of 35°, 45° and 65° (Table 8).

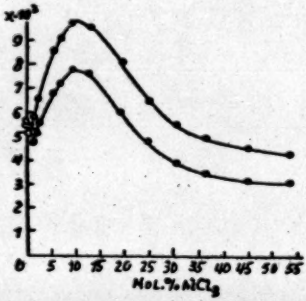

Fig. 5. Specific conductivity of the ICl–$AlCl_3$ system.

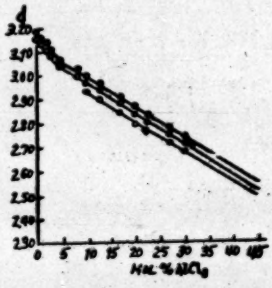

Fig. 6. Specific gravity of the ICl–$AlCl_3$ system.

Table 8

Specific Gravity of the ICl–$AlCl_3$ System

$AlCl_3$ (Mol.%)	35°	45°	65°
ICl	3.184	3.159	–
1.14	3.167	3.131	–
2.05	3.141	3.106	–
2.49	3.115	3.082	–
4.44	3.067	3.042	–
8.11	3.025	2.992	–
9.85	2.989	2.977	2.932
12.77	2.956	2.938	2.912
17.00	2.916	2.887	2.859
20.38	2.871	2.839	2.798
23.99	2.837	2.806	2.764
27.22	2.780	2.759	2.739
29.13	2.748	2.728	2.708

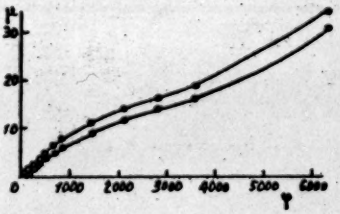

Fig. 7. Molecular conductivity of the ICl–$AlCl_3$ system, based on $AlCl_3$.

The specific-gravity isotherms are almost linear, with a slight concavity at 4 mol.% of $AlCl_3$ (Fig. 6). The molecular conductivity of the ICl – $AlCl_3$ system is listed in Table 9 and Figs. 7 and 8.

Table 9

Molecular Conductivity of the ICl–$AlCl_3$ System

$AlCl_3$ (Mol.%)	35°		45°		ICl (Mol.%)	35°		45°	
	φ	μ	φ	μ		φ	μ	φ	μ
0.00	51.0	0.28	51.41	0.29	100	51.00	0.28	51.41	0.29
0.81	6284	32.24	6333	35.27	99.19	51.64	0.26	52.07	0.28
1.42	3612	16.97	3642	18.98	98.58	52.19	0.25	52.66	0.27
1.79	2829	14.65	2854	16.41	98.21	52.58	0.27	53.00	0.30
2.41	2165	12.06	2184	14.24	97.59	53.06	0.29	53.58	0.35
5.89	904.8	6.06	914.9	7.91	94.11	55.99	0.38	56.55	0.49
7.28	723.6	5.13	729.7	6.68	92.72	57.09	0.40	57.64	0.53
9.44	554.9	4.31	560.5	5.48	90.56	58.83	0.46	59.41	0.58
13.22	404.6	3.04	408.6	3.93	86.78	62.03	0.47	62.56	0.60
19.65	277.7	1.66	280.0	2.25	80.35	65.08	0.40	68.71	0.55
24.77	223.1	1.05	225.7	1.46	75.23	73.66	0.34	74.35	0.48
30.80	182.8	0.71	184.1	0.99	69.20	81.50	0.32	82.26	0.44
36.66	156.6	0.55	156.3	0.79	63.34	90.59	0.32	91.28	0.46
45.04	130.8	0.42	131.9	0.59	54.96	107.24	0.34	108.1	0.48
49.08	122.3	0.39	123.3	0.53	50.92	117.8	0.37	118.7	0.51
53.71	112.5	0.35	113.4	0.46	46.29	130.6	0.41	131.6	0.54

The curves showing the variation of molecular conductivity with dilution differ, depending on how the conductivity is computed. If the conductivity is based on $AlCl_3$, μ rises with dilution, and the curve has a "normal", though somewhat S-shaped character (Fig. 7). If ICl is considered the electrolyte, the variation of μ with dilution is expressed by a curve with an "anomalous" shape, having a maximum and a minimum (Fig. 8). The maximum occurs at about the same $AlCl_3$ concentration as for the isotherms of specific conductivity.

The conductivity minimum occurs at about 30 mol.% of $AlCl_3$, which is very close to $AlCl_3 \cdot 2ICl$.

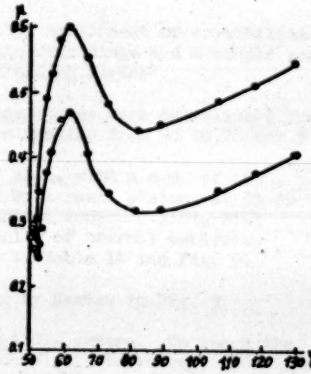

Fig. 8. Molecular conductivity of the ICl–$AlCl_3$ system, based on ICl.

Thermal analysis of the ICl – $AlCl_3$ system. We encountered the greatest difficulty in making a thermal analysis of this system. The reason for the considerable experimental difficulties involved in the investigation of systems

containing $AlCl_3$ or $AlBr_3$ is the extremely high volatility of $AlCl_3$, subliming at temperatures below the melting point, fusing only in a sealed container at 2 atm pressure, and hydrolyzing very easily.

Visual measurement at concentrations below some 10 mol.% of $AlCl_3$ enabled us to obtain critical eutectic points for both the heating and cooling curves (4-5°). From 13 mol.% of $AlCl_3$ (the eutectic) upward, the melt is considerably supercooled. Repeated and intensive chilling was required to bring about crystallization.

This made it possible to measure the critical points for concentrations up to 20 mol.% of $AlCl_3$, for both the heating and cooling curves. At higher concentrations of $AlCl_3$ even greater supercooling was observed; keeping the container for 12 hours at -25°, chilling it with solid carbon dioxide to -50°, and seeding with tiny crystals of ICl or $AlCl_3$ having no effect in producing crystallization of the melt. The melt became thick and viscous, but did not crystallize. This phenomena was observed almost up to 50 mol.% of $AlCl_3$.

A melt left in a sealed container crystallized by itself only after several weeks had passed.

Other difficulties were encountered in our investigation of the system with respect to the other component: $AlCl_3$. A melt (in a sealed container), with a low percentage of ICl, looked like a thick black liquid that did not wet the walls of the container; the heat of crystallization was so small, and the entire mass crystallized so rapidly, all at once, that we were unable to detect any arrest points at all.

The only way we could measure this negligibly small heat of crystallization was with the aid of extremely sensitive photo recordings and a simple and differential thermocouple in N. S. Kurnakov's recording device[1].

The melting points and crystallization temperatures were established from the heating and cooling curves for concentrations ranging from 90 to 28 mol.%.

A second eutectic was found at 42 mol.% of $AlCl_3$ with a m.p. of 105°, and a dystectic with a m.p. of 110°, represented by a small plateau at 35-36 mol.% of $AlCl_3$, which indicates that the coordination compound $AlCl_3 \cdot 2ICl$ formed in this system is unstable. All the results of thermal analysis, obtained visually or photographically, are given in Table 10 and Fig. 9.

The region of intense supercooling is shown by dashes in Fig. 9.

Electrolysis and ion transfer in the $ICl - AlCl_3$ system. To learn the behavior of this system during electrolysis, electrolysis tests were made in a small U-shaped container with platinum electrodes. The runs lasted 2 to 3 hours at currents of 5 to 10 milliamp.

Deposition was exhibited at the cathode and the anode during these tests.

As a rule, a grayish brown deposit, resembling iodine, settled on the cathode, whereas a voluminous dark-brown mass was deposited on the anode. As both of these deposits were impregnated with the initial solution, this solution had to be washed out before they could be investigated. All solvents tried out

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1 The authors wish to convey their profound gratitude to S.D.Shargorodsky for his assistance in this work.

Table 10

Thermal analysis of the ICl–$AlCl_3$ system

$AlCl_3$ (Mol. %)	Critical point		$AlCl_3$ Mol. %	Critical point	
	1	2		1	2
0.00	27.0°	–	36.51	110°	–
2.49	24.0	–	38.16	110	–
4.87	21.5	–	40.55	108	–
7.82	13.5	–	42.14	105	–
10.59	7.0	5.0°	46 56	132	105°
13.31	2.0	–	51.61	138	–
13.98	–	4.5	60.49	155	–
15.88	9.0	5.0	69.50	170	–
18.19	23.5	6.0	80.45	178	–
20.30	32.0	5.0	90.71	186	–
28.55	100.0				

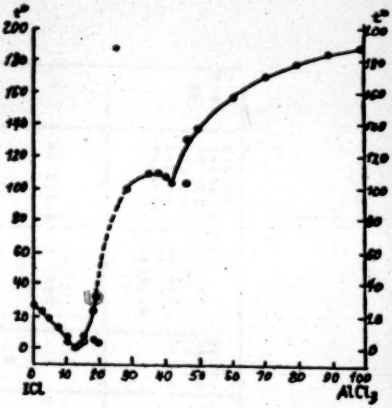

Fig. 9. Fusibility curve for the ICl–$AlCl_3$ system

for this purpose (alcohol, ether, nitro benzene) washed out the solution together with the deposits. Only in chloroform could part of the undissolved anodic deposit be retained, if the chloroform was not used in excess; the cathode deposit, however, washed off in toto, giving the solution the purple color that is characteristic of iodine.

Part of the anodic deposit that did not dissolve in chloroform settled on the bottom of the test tube as a white powder, sometimes in the form of tiny yellow crystals, which likewise changed into a white powder with the passage of time, and at other times as rather large yellow needle crystals.

When we tried to filter these crystals out, they deliquesced in the air, turning into a white, water-soluble powder containing aluminum and chlorine.

Investigation of ion transfer was done both in a three-compartment vessel to separate the solution into cathode, middle, and anode parts (Experiment 2), and in a U-tube with a stopcock in the middle and two branches below to separate the solution being tested into cathode and anode parts after electrolysis.

Platinum electrodes were used. A copper coulometer was connected into the circuit. The tests were run for from 30 to 65 hours. The current was 6 to 10 milliamp.

The ICl-$AlCl_3$ melts were prepared in a flask with a ground-glass stopper.

After the runs, the anode and cathode liquids were separated and analyzed as already indicated [5,6]. It should be stated at this point that iodine and chlorine were lost when the electrolysis liquids were treated with an aqueous solution of SO_2, owing to the intense exothermic reaction.

To eliminate these losses, we dissolved the suspensions of the anode and

Table 8

Ion Transfer in the ICl-KCl System

Test No.	Composition of ICl: KCl solution (moles)	Cu deposited in the coulometer, g	Substance isolated	Solution after electrolysis								
				anode portion			cathode portion			middle portion		
				should read, g	found g	Δ in g	should read, g	found g	Δ in g	should read, g	found g	Δ in g
1	94.5:5.5	0.1780	K	0.2383	0.1750	-0.0633	0.1155	0.1786	+0.0631	0.0849	0.0852	+0.0003
			I	12.9421	13.2033	-0.1306	6.3346	6.4691	+0.1345	4.6589	4.6483	-0.0106
2	94.5:5.5	0.2211	K	0.2210	0.1364	-0.0846	0.2533	0.3402	+0.0869	0.0815	0.0805	-0.0010
			I	12.5566	12.3372	-0.2194	14.3932	14.6125	+0.2193	5.2047	5.2050	+0.0003
			Cl	3.7110	3.9350	+0.2240	4.2538	4.0290	-0.2248	1.5382	1.5384	+0.0002
3	92.3:7.7	0.1517	K	0.3003	0.2568	-0.0435	0.2165	0.2612	+0.0447	0.0894	0.0904	-0.0010
			I	17.4841	17.1951	-0.2890	12.6031	12.8909	+0.2878	5.3044	5.2996	-0.0048
			Cl	4.8609	4.9345	+0.2736	3.6278	3.3555	-0.2723	1.4980	1.4855	-0.0123

Table 11

Ion Transfer in the ICl-$AlCl_3$ System

Test Np.	$AlCl_3$ (mol %)	Cu deposited in the coulometer, g	Substance isolated	Solution after electrolysis									Transference No. based on 1/3 Al	
				cathode portion			middle portion			anode portion				
				should read, g	found g	Δ in g	should read, g	found g	Δ in g	should read, g	found g	Δ in g	Anode portion	cathode portion
1	28.08	0.0270	Al	0.9521	0.9491	-0.0030	-	-	-	0.4398	0.4428	+0.0032	0.390	0.415
			I	11.4688	11.4909	+0.0221	-	-	-	5.2956	5.2669	-0.0287	-	-
			Cl	6.9639	6.9302	-0.0337	-	-	-	3.2155	3.2436	+0.0281	-	-
2	29.55	0.0755	Al	0.6486	0.6402	-0.0081	0.3772	0.3770	-0.0002	0.6382	0.6386	+9.0084	0.378	0.392
			I	11.7950	1.8987	+0.1037	6.8638	6.8542	-0.0004	11.4649	11.3593	-0.1056	-	-

cathode liquids after separation in nitrobenzene, and then treated them with the aqueous solution of SO_2.

The test results are given in Table 11. The data in the table indicate that the percentage of aluminum and chlorine rises in the anode section and falls in the cathode section of the ICl – $AlCl_3$ system, whereas the percentage of iodine increases in the cathode section and rises in the anode section.

Our data indicate the formation of a complex compound in the ICl – $AlCl_3$ system.

The rise in the conductivity of ICl as more of the poor conductor $AlCl_3$ is added is evidently due to the formation of conductive complex molecules; this may explain the rise of the conductivity isotherm to a maximum. The subsequent drop in conductivity is obviously related to an increase in the system's viscosity. Nor is it impossible for the molecules to become associated. The anomalous shape of the curve showing the variation of molecular conductivity with dilution justifies the assumption that the complex molecules responsible for the system's conductivity break down at a given dilution value.

The thermal analysis, which revealed a dystectic near 35 mol.% of $AlCl_3$, indicates the formation of an unstable compound with the formula $AlCl_3 \cdot 2ICl$.

The experiments undertaken to investigate ion transfer in the ICl–$AlCl_3$ system entailed considerable experimental difficulties: we were unable to take a ratio of ICl to $AlCl_3$ for these tests that corresponded to the complex disclosed in the fusibility diagram, since the ICl–$AlCl_3$ system has a high melting point, 110°, at 33-35 mol.% $AlCl_3$. Experiments with a supercooled solution involved the possibility of large errors. We therefore had to take a melt that contained an excess of iodine chloride over the $2ICl:AlCl_3$ proportion indicated above. As a result, the electrolysis of the complex compound formed in the ICl–$AlCl_3$ system is paralleled by the electrolysis of the excess iodine chloride.

The simultaneous electrolysis of the iodine chloride and the coördination compound formed in the ICl–$AlCl_3$ system, and the relatively low stability of this compound, complicated the quantitative description of the ion-transfer tests in the ICl–$AlCl_3$ system considerably.

As a result, we had to limit ourselves in the main to a qualitative characterization of these investigations, which indicated that aluminum enters the anion of the coördination compound, whose cation in all probability is iodine.

In this respect our results agree with the conclusions reached in the investigation of ion transfer in the ICl–$AlCl_3$–$C_6H_5NO_2$ system [5].

The fairly good agreement for the transference number of aluminum found in the two experiments testifies to the reproducibility of the results. It

should also be noted that this transference number is close to the values obtained for nitrobenzene solutions [5].

As for the problem of the structure of the coordination compound formed in the ICl – $AlCl_3$ system, we have not finally resolved this question as yet.

If it is held that the co-ordination compound $2ICl \cdot AlCl_3$ detected by thermal analysis remains unchanged in the liquid phase as well, it may be supposed that we have here the co-ordination compound $ICl \cdot AlCl_3$ (or $IAlCl_4$), solvated with another molecule of ICl.

Nor is the assumption without foundation that a co-ordination compound of simpler composition, namely, $ICl \cdot AlCl_3$, exists in the liquid phase, a co-ordination compound like the one discovered by one of the present authors on the viscosity isotherm of the analogous system IBr – $AlBr_3$.

In any event, it may be asserted that a co-ordination compound of ICl and $AlCl_3$, like the compound of IBr and $AlBr_3$, cannot be classed with the polyhalogenides. It must be considered a double halogenide, the $AlCl_3$ constituting the anion of this co-ordination compound. For the simplest of these compounds (equimolar composition) we may assume the structure represented by $I[AlCl_4]$.

SUMMARY

1. Investigation of KCl – ICl system confirmed the formation of a co-ordination compound of potassium chloride and iodine chloride in this system, the composition and structure of which may be expressed as $K[ICl_2]$.

2. Investigation of the $AlCl_3$ – ICl system indicated that $AlCl_3$ forms a relatively unstable co-ordination compound with ICl. The formula $2ICl \cdot AlCl_3$ must be assigned to this compound according to the results of thermal analysis. It is possible that in the liquid phase a simpler compound, $ICl \cdot AlCl_3$, exists. The results of study of ion transfer in the ICl–$AlCl_3$ system suggest the possibility of taking $I[AlCl_4]$ as the structure of this compound.

3. The co-ordination compounds of ICl with KCl or $AlCl_3$ should be classed as binary halogenides.

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RESEARCH INTO THE THERMAL STABILITY AND VOLATILITY OF THE NORMAL SULFATES OF THE ALKALI ELEMENTS

Vict. I. Spitsyn and V. I. Shostak

M. B. Lomonosov Laboratory of Inorganic Chemistry of the Moscow State University awarded the Order of Lenin

The literature data on the thermal stability and volatility of the normal sulfates of the alkali elements are very limited and often contradictory.

Jaeger [1] points out that lithium sulfate decomposes at 1200°. The calcination residue exhibits an alkaline reaction after being wetted with water. Dissociation was observed by this author at 1100° and 1550° for sodium and potassium sulfate, respectively. According to Boussingault [2], sodium and potassium sulfates volatilize at "white heat". Cobb [3] found that sodium sulfate begins to decompose, evolving fumes of sulfur trioxide, in the temperature range 1200-1220°. More marked decomposition occurs at 1330-1350°.

Rubidium sulfate, according to various authors [1,3], volatilizes visibly at about 1400°. Cesium sulfate proved to be nonvolatile at its melting point [4], beginning to evaporate at about 1325°, this process becoming intense at 1440° [1].

Fialkov and Shargorodsky [5] used the heats of formation to calculate the theoretical temperatures at which the pressure of the dissociation products of the sulfates of the alkali elements is 1 atmosphere, obtaining the following results: LI_2SO_4 1748.0°, Na_2SO_4 2177.7°, K_2SO_4 2637.0°, Rb_2SO_4 2640.0°, and Cs_2SO_4 2635.0°.

There is no mention in the literature of a relationship between the stability or volatility of the sulfates and their melting points or the ionic radii of the respective alkali elements.

The present report deals with the calcination behavior of the sulfates of all the alkali elements, determining the temperatures at which they begin to lose weight, as well as with changes in the composition of the sulfates upon calcination, the degree of their thermal decomposition, and their rates of evaporation under comparable conditions.

The required sulfates were prepared as follows. Normal lithium sulfate was produced by the action of the computed quantity of sulfuric acid upon lithium carbonate. The crystals formed when the solution was evaporated were calcined at 500-600° until their weight remained constant.

The sodium and potassium sulfates used were the commercial preparations, marked "chemically pure." They were analyzed after recrystallization and calcination at 800°. The sulfates of rubidium and cesium were prepared by evaporating a solution of the respective chlorides with a slight excess of sulfuric acid over what is required for producing the normal sulfate. The dry residue was calcined at 700-800° until constant weight was attained.

The analyses of the substances thus prepared are listed in Table 1.

The thermal stability and volatility of the alkali sulfates at high temperatures were investigated in a tubular furnace without passing air through the operating tube. The weighed sample of the preparation was in a platinum boat, placed in another closed platinum box.

The results of calcining the sulfates of the alkali elements at various temperatures are shown in Table 2.

Table 1

Analysis of the Substances Used in Studying the Thermal Stability and Volatility of the Sulfates of the Alkali Elements

Compound	Percent of SO_3	
	Found	Theory
$LiSO_4$.....	72.68	72.77
Na_2SO_4.....	56.39	56.34
K_2SO_4.....	45.76	45.95
Rb_2SO_4.....	29.90	29.98
Cs_2SO_4.....	22.18	22.14

At 800° none of the sulfates exhibited any change in weight. At 900° a negligible loss of weight was observed for the sulfates of lithium, rubidium, and cesium. At 1000° the sulfates of all the alkali elements suffer a loss of weight, sodium and potassium sulfates suffering the least loss. It may be added that when the calcining temperature was raised to 1100°, the loss of weight was multiplied many times.

For the sulfates of lithium and sodium, a noticeable loss of weight sets in at 50-100° above the melting point. For potassium, rubidium, and cesium, the temperature at which loss of weight sets in is 70° to 170° below the melting points of these compounds. It should be noted that the correlation of the temperatures at which loss of weight sets in during calcination of these sulfates differs from the correlation of their melting points: sodium and potassium sulfates have the highest temperatures at which loss of weight begins, whereas the highest melting points are those for potassium and rubidium sulfates.

Table 3 shows the changes in the weight of the sulfates of all the alkali elements at 1200° in air.

Sodium sulfate suffers the smallest loss of weight under identical temperature conditions. The changes in weight for lithium and potassium sulfates are very close to each other. The loss of weight is found to be much higher for rubidium sulfate, and especially for cesium sulfate.

Some of the sulfates were used in a study of the effect of a current of air upon the magnitude of the loss of weight during calcination. As the figures in Tables 4 and 5 indicate, the loss of weight rose but little for the sulfates of lithium and sodium under these conditions. A current of air has a greater effect upon the increase in the loss of weight for potassium sulfate, and especially so for cesium sulfate.

Table 2

Calcination of the Sulfates of the Alkali Elements at Different Temperatures

Calcination Time = 2 hours

Compound	Temperature °C	Initial weight	Loss of weight	
			g	%
Li_2SO_4	800	0.2573	none	–
	900	0.2573	0.0003	0.12
	1000	0.2570	0.0013	0.51
Na_2SO_4	800	0.2492	none	–
	900	0.2492	none	–
	1000	0.2491	0.0001	0.04
K_2SO_4	800	0.2518	none	–
	900	0.2518	none	–
	1000	0.2518	0.0003	0.12
Rb_2SO_4	800	0.2581	none	–
	900	0.2581	0.0002	0.08
	1000	0.2579	0.0007	0.27
Cs_2SO_4	800	0.2535	none	–
	900	0.2535	0.0005	0.20
	1000	0.2530	0.0022	0.87

Table 3

Calcination of the Sulfates of the Alkali Elements at 1200°

Calcination Time = 2 hours

Compound	Initial weight, g.	Loss of weight		Calculated average loss of weight per hour of calcination, %
		g	%	
Li_2SO_4	0.2612	0.0092	3.52	1.76
Na_2SO_4	0.2669	0.0028	1.05	0.52
K_2SO_4	0.2608	0.0095	3.64	1.82
Rb_2SO_4	0.2620	0.0165	6.29	3.14
Cs_2SO_4	0.2650	0.0368	13.89	6.94

It should also be noted that increasing the airstream velocity from 0.2 to 0.4 liters/min causes the loss of weight to drop instead of rising, possibly because of the cooling of the surface of the fused sulfate by the current of gas.

Investigation of the composition of the residue of sulfate calcination at 1200° yielded the following results. It was found that lithium and sodium sulfates exhibited a considerable decrease in their percentage of SO_3 after the

Table 4

Calcination of Sulfates of the Alkali Elements in A Current of Air

Temperature = 1200°. Calcination Time = 30 min.

Compound	Air stream speed, liters per min.	Initial weight in g	Loss of weight		Calculated average loss of wt. per hour of calcination, %
			g	%	
Li_2SO_4 ..	0.2	0.2492	0.0032	1.28	2.56
	0.4	0.2539	0.0018	0.71	1.42
Na_2SO_4 ..	0.4	0.2552	0.0008	0.31	0.62
K_2SO_4 ..	0.2	0.2540	0.0047	1.85	3.70
	0.4	0.2530	0.0035	1.38	2.76
Cs_2SO_4..	0.2	0.2476	0.0771	31.14	60.26
	0.2	0.2483	0.0723	29.12	

test. The calcination residue gave an alkaline reaction when moistened with water. The composition of the potassium, rubidium, and cesium sulfates remained unchanged, within the limits of experimental accuracy, the aqueous solutions of the respective calcination residues exhibiting a neutral reaction.

As the figures in Table 6 indicate, lithium and sodium sulfates doubtless undergo decomposition at the temperature employed, in accordance with the following equation:

$$Me_2SO_4 \rightleftharpoons Me_2O + SO_3.$$

Evidently, both of the oxides formed can evaporate at the high temperature of the test, but the evaporation rate of sulfur trioxide is much higher than that of an alkali-element oxide. Moreover, alkalin oxides apparently tend to dissolve in the remaining undecomposed salt. As for the sulfur trioxide, we must also take into account its decomposition at high temperatures into sulfur dioxide and oxygen. We established the fact qualitatively that air, previously purified, contained sulfur dioxide after having passed over a weighed batch of lithium sulfate at 1200°; the sulfur dioxide can be absorbed in water or in a solution of iodine in potassium iodide.

Table 5

Comparison of Losses of Weight of Sulfates of the Alkali Elements During Calcination in Air and in a Current of Air.

Temp. = 1200°; Wt. of Samples About 0.25 g

Compound	Air stream speed, l/ min.	Calculated average loss of weight per hour of calcination, %	
		In air	In a current of air
Li_2SO_4..	0.2	1.76	2.56
Na_2SO_4..	0.4	0.52	0.62
K_2SO_4...	0.2	1.82	3.70
Cs_2SO_4..	0.2	6.94	60.26

The changes in weight and in the composition of the calcined sulfates were used to calculate the degree of their decomposition and the evaporation rates. The results of computation are given in Table 7, recalculated on the basis of 1 hour of calcination for convenience in comparison.

Table 6

Analysis of the Residues of the Sulfates of the Alkali Elements After Calcination at 1200°

Compound	Calcination time, hours	Initial weight, g	Loss of Weight		Per cent SO_3		Reaction of aqueous solution of calcination (against methyl red).
			g	%	Initially	In calcination residue.	
Li_2SO_4	6	0.2648	0.0240	9.06	72.68	71.49	Alkaline
	8	0.2583	0.0330	12.78	72.68	71.07	
Na_2SO_4	12	0.2630	0.0280	10.65	56.39	55.70	Weakly alkaline
K_2SO_4	8	0.2486	0.0339	13.64	45.76	45.73	Neutral
Rb_2SO_4	8	0.3130	0.0700	22.36	29.90	30.00	Neutral
Cs_2SO_4	2	0.2543	0.0306	12.06	22.18	22.32	Neutral
	2	0.2483	0.0401	16.15	22.18	22.09	

It should be noted that the loss of weight observed for lithium and sodium sulfates exceeds the figure computed from the decrease in the percentage of SO_3. Thus, the direct evaporation of the compounds takes place alongside their decomposition. Moreover, it is not impossible that some of the initial products of the decomposition of these sulfates (Me_2O and SO_3) are eliminated from the weighed batches used in equivalent quantities; hence, the degrees of decomposition given in Table 7 for lithium and sodium sulfates are probably somewhat too low, since they are based on the change in the composition of the calcination residue and made no allowance for the amounts of sulfur trioxide and alkali oxide that evaporate together after their formation during the decomposition of the sulfates.

The probable reason for the thermal instability of lithium and sodium sulfates in the high-temperature regions investigated is the development of counterpolarization in these compounds.

The SO_4^{-2} anion must be under unusual pressure owing to the unilateral polarization of the oxygen ions by the central sulfur atom. The lithium ion, which is small, induces counterpolarization of the oxygen ions, which facilitates the decomposition of lithium sulfate to its oxide. The phenomenon of counterpolarization is exhibited much more weakly in sodium sulfate, owing to the large ion radius of sodium. It is practically not present in potassium sulfate; this is even more true of rubidium and cesium sulfates. That is why these substances prove to be stable under the experimental conditions. It should not be considered an exception, however, that thermal dissociation also occurs at 1200° in the case of the sulfates of the heavy alkali elements, but the dissociation products may possibly evaporate in strictly equivalent quantities, owing to the high volatility of the oxides of potassium, rubidium, and cesium.

Table 7

Degree of Decomposition and Rate of Evaporation of Sulfates of the Alkali Elements at 1200°

Weight of Samples = 0.25-0.30 g (Table 6)

Compound	Calcination time, hours	Changes During Test			Computed change during 1 hour			
		Degree of decomposition, %	Evaporation		Degree of decomposition, %	Evaporation rate		
			g	%		g	%	Millimoles
Li_2SO_4	6	5.18	0.0140	5.28	0.86	0.0029	0.88	0.021
	8	6.96	0.0199	7.69	0.87	0.0025	0.96	0.023
Na_2SO_4	12	2.51	0.0243	9.24	0.21	0.0020	0.77	0.014
K_2SO_4	8	none	0.0339	13.64	none	0.0042	1.70	0.024
Rb_2SO_4	8	none	0.0700	22.36	none	0.0087	2.79	0.033
Cs_2SO_4	2	none	0.0368	13.89	none	0.0184	6.94	0.051

Table 8

Calcination of the Sulfates of the Alkali Elements in a Current of Steam at 1200°

Rate of Steam Flow = 18 g/hour. Internal Diameter of Porcelain Tube Employed = 20 mm.

Compound	Calcination time, hours	Initial weight g	Loss of weight		Computed loss of weight per hour calcination	Per cent SO_3		Reaction of aqueous solution of calcination residue (against methyl red)
			g	%		Before	After	
Li_2SO_4	0.5	0.2500	0.0219	8.76	17.52	72.68	71.63	Alkaline
Na_2SO_4	2.0	0.2533	0.0187	7.38	3.69	56.39	56.05	Weakly alkaline
K_2SO_4	1.0	0.2516	0.0296	11.76	11.76	45.76	45.57	Neutral
Rb_2SO_4	0.5	0.1830	0.0370	20.22	40.44	29.90	30.14	Neutral
Cs_2SO_4	0.5	0.2010	0.1016	50.55	100.00	22.18	22.22	Neutral

To check this assumption the sulfates of the alkali elements were subjected to calcination at 1200° in a current of steam to intensify their decomposition by the action of hydrolysis and to increase the amount of alkali remaining as a residue after a weighed portion of the sulfate had been calcined. The results of these tests are given in Table 8.

Table 9

Comparison of Degree of Decomposition and Evaporation Rate of the Sulfates of the Alkali Elements in Air and in a Current of Steam

Compound	Computed change per hour of calcining					
	Total loss of Weight, %		Degree of decomposition		Weight loss due to decomposition	
	In air	In current of steam	In air	In current of steam	In air	In current of steam
Li_2SO_4..	1.76	17.52	0.86	4.78	0.92	10.84
Na_2SO_4..	0.52	3.69	0.21	0.31	0.77	3.34
K_2SO_4...	1.82	11.76	none	none	1.70	11.76
Rb_2SO_4..	3.14	40.44	none	none	2.79	40.44
Cs_2SO_4..	6.94	90.85	none	none	6.94	90.85

A change in the composition of the residue, as against the initial substance, and the appearance of an alkaline reaction after calcination in a current of steam are found to exist only in the lithium and sodium sulfates, as was the case in the experiments with air. The degree of decomposition of the lithium and sodium sulfates, computed from the change in composition, as well as the evaporation rate of all the sulfates, when calcined in air and in a current of steam are compared in Table 9.

As the figures show, the loss of weight exhibited by the sulfates of the alkali elements when calcined in a current of steam is much greater than that suffered by them in air. This is a 10 to 13-fold increase in the case of the lithium, rubidium, and cesium sulfates, and a sixfold to sevenfold increase for sodium and potassium sulfates.

Only in the case of cesium sulfate does an increase in the evaporation rate in a current of air (0.2-0.4 liters/min) and in a current of steam (18g/h) over calcination in air yield approximately the same results. For the other sulfates, calcination in a current of steam exhibits a considerable increase in loss of weight over calcination in a current of air. This increase is 6 to 7-fold for lithium and sodium sulfates, and 1.5 to 3-fold for potassium and cesium sulfates.

The degree of decomposition of lithium sulfate in a current of steam is more than 5 times that suffered during calcination in air. The increase in the decomposition of sodium sulfate is less marked, about 50%.

From this we may conclude that, for sulfates whose decomposition is hardly observable, calcination in a current of steam makes it possible actually to increase decomposition, thus making it easier to detect. Once again, this confirms the conclusion that the sulfates of potassium, rubidium, and cesium do not suffer thermal decomposition at 1200°, merely evaporating under these conditions.

Thus, these experiments enable us to state with assurance that the sulfates of all the alkali elements can evaporate at high temperature without suffering changes in composition. The sulfates of lithium and sodium also exhibit the phenomenon of thermal decomposition.

Under identical experimental conditions, the evaporation rates of the sulfates of the alkali elements diminish from lithium to sodium, rising again as we proceed to potassium, rubidium, and particularly, cesium. Calcination of the sulfates in a current of steam follows the same sequence as the volatility. It should be borne in mind that the minimum temperature at which weight loss occurs (900°) was found for the sulfates of lithium, rubidium, and cesium, whereas the corresponding temperature is higher (1000°) for sodium and potassium sulfates (Table 2).

The order of volatility of the sulfates of the various alkali elements depends, primarily, on various factors.

First, it must be said that the sulfates of potassium, rubidium, and cesium, which have the highest melting points (1074, 1074, and 1019°, respectively) of the normal alkali sulfates, are likewise distinguished by the lowest volatility. It should also be noted that, notwithstanding the closeness of the melting points of potassium, rubidium and cesium sulfates, the evaporation rates of these compounds are quite different under identical conditions, this ratio being 1:1.4:2.1 at 1200° when the molecular values of weight loss are compared (Table 7).

From this it may be concluded that evaporability depends not so much upon the ionic interactions that occur in the crystal lattice of the sulfate, as upon the change in form of the chemical bond that occurs in the sulfates during fusion and subsequent heating. Evidently, the maximum coupling forces in the crystal lattice change sharply with weakening molecular coupling forces in the decomposing substance.

This phenomenon may be ascribed apparently, as one of the present authors has done with regard to the normal wolframates of rubidium and cesium [8], by the polarizability of the alkali elements under the action of oxygen ions contained in the SO_4^{-2} anion. This polarization phenomenon may be hardly noticeable in salts of lithium, but it ought to increase as we pass to the alkali elements with larger ion radii, particularly rubidium and cesium. A consequence of this phenomenon will be a shift of the chemical bond between the ion of the alkali element and the SO_4^{-2} radical from an ionic bond to a polar one, resulting in the increase in the compound's volatility observed when we pass from sodium sulfate to the sulfates of potassium, rubidium, and cesium. Unlike the normal wolframates of rubidium and cesium, this phenomenon of polarization affects only the volatility of the sulfates within the temperature range investigated, having no effect upon their stability. This apparently depends upon the highly monolithic nature of the SO_4^{-2} ion as compared to the WO_4^{-2} ion.

The increased volatility of lithium sulfate, like its lower melting point, compared to the sulfates of the other alkali elements is evidently related to the polarizing action of the lithium ion upon the SO_4^{-2} ion, and the corresponding reduction of the ionic nature of the bond between them.

It must be assumed that in the fused state sodium sulfate is a compound of a more ionic type than the sulfates of the other alkali elements. The polarizing action of the sodium ion upon the SO_4^{-2} ion is considerably less than that of the lithium ion, and its polarizability under the action of the SO_4^{-2} ion or of the oxygen ions contained in the latter is not as great as in the ions of potassium, rubidium, and cesium. Accordingly, sodium sulfate is the least volatile of all the alkali-element sulfates at given temperatures (say, at 1200°).

SUMMARY

1. The thermal stability and volatility of the normal sulfates of all

the alkali elements were studied.

At 800° none of the sulfates investigated exhibited any change in weight. Beginning with 900°, a slight loss of weight is noticed for the sulfates of lithium, rubidium, and cesium, and at 1000° for the sulfates of sodium and potassium. As the temperature is raised still higher, the weight loss rises sharply for all the sulfates.

2. A change in the composition of the residue is observed (reduction of the SO_3 percentage) for the sulfates of lithium and sodium after calcination in air at 1200°.

3. Under the same temperature conditions the sulfates of all the alkali elements tend to evaporate directly. Volatility increases as we pass from the lithium salt to the cesium salt.

4. The effect of a current of steam upon the evaporation rate of alkali sulfates at 1200° was investigated. The observed weight loss increased 6 to 7 times for the lithium and sodium salts and 1.5 to 3 times for the potassium and cesium salts over the values found in the experiments made with a current of air. Only the sulfates of lithium and sodium suffered a change in the composition of the residue after calcination.

The degree of decomposition of lithium sulfate in a current of steam is more than five times as high as in air, this increase being much less pronounced – about 50% – for the sodium salt.

5. The thermal instability of the lithium and sodium sulfates is ascribed to the phenomenon of counter-polarization in the molecules of these compounds. This is also the reason for the higher volatility of lithium sulfate.

6. The rise in the volatility of the alkali sulfates as we pass from sodium to cesium is probably due to the polarization of the ions of the alkali elements by the oxygen ions in the SO_4^{-2} anion. The polarizability of the alkali-element ions increases with the radius of the cation and may be the result of the change in the form of the chemical bond within the compound from an ionic one to a polar one, which ought to be related to the increased volatility.

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COBALT-THIOCYANOGEN COMPLEX GROUPS IN SOLUTION

A. K. Babko and O. F. Drako

Institute of General and Inorganic Chemistry of the
Ukrainian Academy of Sciences

Very many papers have been published on colored thiocyanogen (and chloride) complex ions with cobalt in solution. Study of the properties of solutions of these complex ions has often served as the touchstone for various theories, such as the hydrate theory (Potylitsin [1] and others), according to which the color of the solid salt and of its solution depends upon the degree of hydration of the molecule.

Most research workers ascribe the blue color of the solution to the formation of complex ions of the CoR_3^- or CoR_4^{--} type, with the expulsion of water from the inner sphere of the molecule. Hantzsch [2] is of a somewhat different opinion, having obtained a number of addition products of water, pyridine, quinoline, and other additives to cobalt halogenides ($CoCl_2$ and $CoBr_2$). Compounds that had only two additives were colored blue, whereas compounds that contained 4 and 6 additives (including $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6NH_3$) were colored red and pink.

This leads Hantzsch to think that blue salts do not contain $CoCl_4^{--}$ anions, since the color changes from blue to red when the number of additives increases. Hantzsch's results may be explained quite differently, however. Evidently, additives such as pyridine, water, ammonia, etc. displace the halogen ion from the inner sphere of the complex molecule, and this rupture of the coördination bonds between the Co^{++} and the halogenide (the latter being forced out to the outer sphere) is responsible for the shift from blue salts to red ones.

Despite the large number of papers, despite the various solvents and admixtures, etc., employed, there has been no systematic investigation up to now of the equilibria between the reacting components (Co^{++} and CNS^-) in the solution. The formation of colored complex anions ($CoCl_4^{--}$ or $CoCl_3^{--}$) was shown by ion transfer (Donnan and Basset [3]). Nonetheless, the conditions of formation and the composition of the complex ions were not established directly. Solutions of thiocyanogen complex ions of cobalt are not infrequently used to demonstrate equilibria, but the equilibrium principle itself has been but little emplcyed in studying these solutions.

In accordance with the views set forth above [4], the system may be represented by a ternary diagram (Fig. 1), all the possible relationships and

absolute concentrations of the reacting ions come together in the upper section of the triangle. For example, the geometrical locus of $Co(CNS)_2$ solutions of various concentrations may obviously be represented by the $Co(CNS)_2 - S$ lines. Parenthetically, this sort of section does not characterize equilibrium of coördinate-compound formation as a whole, since the region of predominant existence of several coördinate compounds lie off to a side of this line.

In accordance with general conditions, the equilibrium diagram should look as follows (Fig. 1), if it is assumed that no complex ions that are more complicated are formed. When the cobalt salt is present in excess, the following equilibrium is established:

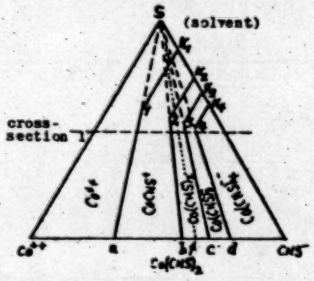

Fig. 1

$$Co^{++} - CNS^- \rightleftarrows CoCNS^+,$$

the first complex group predominating in the solution only at a certain concentration of the thiocyanogen, in accordance with stoichiometric proportions. Thus, for $[CoCNS^+] > [Co^{++}]$, it is necessary that $[CNS^-] \geq 1/2[Co^{++}_{tot.}]$. The stoichiometrical quantity of thiocyanogen will be sufficient to convert a large part of the $[Co^{++}_{tot.}]$ into the complex group $CoCNS^+$ only if the concentration of $C_{compl.}$ is higher than the numerical value of the dissociation constant, $K_1 = \frac{[Co^{++}][CNS^-]}{[CoCNS^+]}$

In dilute solutions (i.e., in the upper portion of the triangle), it may happen that $C_{compl.} < K_1$, and then a certain excess of free thiocyanogen will be required to bind a large part of the cobalt in the complex group $CoCNS^+$. For this reason the boundary of the region in which $CoCNS^+$ predominates (when $C_{compl.} > K_1$) first follows the line $\underline{a} - 1$, later (when $C_{compl.} < K_1$) following the line $1 - K_1$; this latter section is parallel to the triangle side $Co^{++} - S$ and corresponds to $[CNS^-] = K_1$ (see [4] for detailed computations). Similarly, the boundary between the regions in which $CoCNS^+$ and $Co(CNS)_2$ predominate must be expected to lie along the line $\underline{b} - 2 - K_2$, etc. (Fig. 1). At very low dissociation constants (such as occur in acetone solutions), the K_1K_2 points are shifted considerably upward (into the region of extremely dilute solutions), and the boundaries of the regions in which the individual complex groups predominate approach the straight lines $\underline{a} - S$, $\underline{b} - \underline{S}$, etc.

It is the object of the present investigation to apply the principles of physicochemical analysis of solutions to the Co^{++} solution CNS^- solution system. The principal cross sections of Fig. 1, which generally characterize equilibrium in the formation of coördination compounds, are considered below.

Acetone was used as the solvent[1], since it is most frequently employed in the colorimetric determination of cobalt as a thiocyanogen complex group. Individual tests indicated that there are no noticeable signs of dissociation of the complex group in acetone solutions (even with 5-7% of water present). It had been previously established [5] that when the coördination compound

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1 The problem of the effect of other solvnts upon the color of cobalt-thiocyanogen complex groups will be discussed in a separate paper.

dissociates appreciably upon dilution of its solution, a departure from Beer's law occurs. When the solution is diluted n times, the concentration of the light-absorbing groups is reduced more than n times, since the degree of dissociation rises with dilution. We tested the behavior of the system of Fig. 1. in dilutions of various solutions, with a Co^{++}: CNS^- ratio ranging from 4:1 to 1:10; no departure from Beer's law was observed with dilutions of 2,4,8,16, and even 32 times.

Thus, there is no ground for the opinion that a cobalt-cyanogen ion group dissociates in an acetone solution, nor can dissociation be taken as the explanation for certain peculiarities of solutions in the Co^{++} $-CNS^-$ $-$ S system.

Cross Section of the Triangle Parallel to the

Co^{++} $-$ CNS^- Side

This cross section corresponds to a series of experiments made with mixed acetone solutions of Co^{++} and CNS^- of like molarity ($5 \cdot 10^{-2}$ mole) in varying proportions, for constant voluem (Job method).

The initial solutions employed were: 1) a solution of $Co(NO_3)_2$ in acetone; the titer of the solution was determined gravimetrically (weighing in the form of $CoSO_4$); and 2) a solution of NH_4CNS or KCNS in acetone;[1] the titer of the solution was determined argentometrically.

Measurements were made with a Pulfrich photometer with light filters whose transmitted wave lengths are given in Tables 1 – 3.

Table 1

Test No	Co^{++}:CNS^- ratio in mixture	$5 \cdot 10^{-2}$ mole of Co^{++} (in ml)	$5 \cdot 10^{-2}$ mole of CNS^- (in ml)	$\log_e I_0/I$				for 530 m
				At λ=650mμ	At λ=570 mμ	At λ=530 mμ	At λ=500 mμ	
1	4:1	3.2	0.8	0.27	0.46	0.54	0.55	0.37
2	3:2	2.4	1.6	0.52	0.70	0.66	0.60	0.51
3	1:1	2.0	2.0	0.70	0.92	0.70	0.52	0.58
4	1:2	1.34	2.66	1.10	1.22	0.64	0.46	0.56
5	1:3	1.00	3.0	1.22	1.10	0.52	0.42	0.46
6	1:4	0.80	3.20	1.22	1.05	0.35	0.34	0.30
7	1:6	0.57	3.43	1.19	0.82	0.28	0.25	0.25
8	1:9	0.40	3.6	1.0	0.66	0.24	0.21	0.21

Below we give the results of our investigation of optical density as a function of the volumetric proportions of acetone solutions of $5 \cdot 10^{-2}$ molar solutions of Co^{++} and CNS^- for a constant volume of 4 ml and a thickness of 4 mm.

When we examine the figures on any horizontal line, we see that in the absorption spectra the maximum absorption shifts toward the longer wavelengths

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[1]

as the thiocyanogen concentration is increased. In evaluating the composition of the ion group, however, it is important to examine the results in the vertical columns, i.e., the change in intensity of absorption (in various regions of the spectrum) as constitution varies.

The results listed in Table 1 clearly show some complex ion groups formed as the result of the interaction of Co^{++} and CNS^-; a single solution series indicates an absorption maximum for various Co^{++}:CNS^- ratios, depending upon what region of the spectrum was used in the measurement.[1]

In the spectrum region around 530 mμ, (cf. Col. 7, Table 1) the maximum extinction is obtained at a Co^{++}: CNS^- ratio of 1:1. In this region considerable light is absorbed by a solution of cobalt nitrate; that is why a more accurate computation requires that the extinction of cobalt nitrate be deducted from the extinction of a mixture of the salts of cobalt nitrate and ammonium thiocyanate, both taken in the same concentrations. This latter value was measured separately, and the difference (i.e., the deviation from additivity) is listed in Col. 9 of Table 1 (the quantity Δ). To facilitate comparison of results, the variation of Δ as a function of the ratio of the reacting components is plotted as Curve 2 in Fig. 2. Curve 2 has a maximum at Co^{++}: CNS^- = 1:1. Thus, the change in the optical density of the solution caused by the reaction of the $Co(NO_3)_2$ with the ammonium thiocyanate is a maximum under the conditions that correspond to the formation of the complex cation $CoCNS^+$. When cyanogen is present in excess, the color grows much weaker in this region of the spectrum, i.e., the complex $Co(CNS)^+$ initially formed disappears as more of the thiocyanate is added, turning into $Co(CNS)_2$, etc. In the 570 m μ region the color is a maximum at Co^{++}:CNS^- = 1:2. In the region around 650 mμ, where the blue thiocyanogen ion group is more intensely absorbent than anywhere else, the absorption maximum is found at Co^{++}: CNS^- = 1:4 (cf. Table 1, Col. 5, and Fig. 2, curve 1). This latter result (which agrees with the following one), indicates that the blue ion group whose formation is the basis for the well-known qualitative reaction for Co^{++} and its colorimetric determination, is $Co(CNS)_4^{--}$.

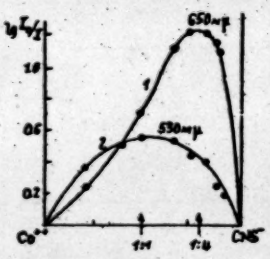

Fig. 2

At the same time it is obvious that the formation of this ion group is not effected directly by the reaction $Co^{++} + 4CNS^- = Co(CNS)_4^{--}$, but rather via a series of intermediate ion groups with a lower number of coordinated thiocyanogen ions. The results can be fully elucidated by a consideration of cross section b in Fig. 1. At low dissociation of the ion group, the cross section of the triangle along a line parallel to the $Co^{++} - CNS^-$ passes through the region in which a number of ion groups predominates. That is why determination of the composition of the ion group by the Job method, as stated above, depends upon choosing the property of the system that is suitable for use as a parameter, as well as upon the importance of this property for the individual components. Thus, measurement of the same series of solutions in a spectrum region of shorter wavelength (around 530 m μ) indicates the formation of the $CoCNS^+$ complex, which

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[1] We studied similar series of solutions with a spectrometer and from the results of absorption in various spectrum regions plotted curves showing the variation of extinction with the ratio of the reacting components. Exhaustive consideration of these data would require too much space; the results fully agree with those set forth in the text.

absorbs light intensively in the very region of the spectrum. Comparison of the extinction in the long wavelength region of the spectrum (at 650 mμ) yields an extinction maximum for solutions that correspond to the right-hand region of the triangle in Fig. 1.

Triangle Cross Section Parallel to the Acetone – CNS^- Side

This cross section corresponds to a series of solutions containing a constant concentration of Co^{++} (10^{-2} mole) and a varying concentration of thiocyanogen. The results of the investigation of such solutions are listed in Table 2.

Table 2

Test No.	$Co^{++}:CNS^-$ ratio in mixture	CNS^- concentration, moles	$\log_e f_o/I$			
			At λ = 650 mμ	At λ = 570 mμ	At λ = 530 mμ	At λ = 500 mμ
1	2	3	4	5	6	7
1	20:1	$5 \cdot 10^{-4}$	0.03	0.09	0.12	0.12
2	5:1	$2 \cdot 10^{-3}$	0.05	0.14	0.18	0.17
3	2:1	$5 \cdot 10^{-3}$	0.22	0.30	0.36	0.30
4	1:1	10^{-2}	0.49	0.66	0.60	0.35
5	1:2	$2 \cdot 10^{-2}$	1.05	1.12	0.60	0.29
6	1:3	$3 \cdot 10^{-2}$	1.35	1.15	0.51	0.21
7	1:4	$4 \cdot 10^{-2}$	1.52	1.19	0.21	0.11
8	1:8	$8 \cdot 10^{-2}$	1.52	1.15	0.21	0.11
9	1:20	$2 \cdot 10^{-1}$	1.52	1.15	0.21	0.11

In general, these results are in agreement with the preceding data. In the 500-530 mμ region (Cols. 6 and 7), the color increases in intensity as the quantity of thiocyanogen rises to 1 and 2 gram-ions per gram-ion of Co^{++}, the color growing paler as more thiocyanogen is added. Thus, the ion groups $CoCNS^+$ and $Co(CNS)_2$ formed initially (with an absorption maximum in the green region of the spectrum) disappear, being converted into $Co(CNS)_3$ and $Co(CNS)_4^{--}$, which are characterized by absorption in the red region of the spectrum. Addition of the thiocyanate in quantities that exceed 4 gram-ions per gram-ion of Co^{++} causes no noticeable change. This indicates the absence of other ion groups with coordination numbers above 4; moreover, it confirms the data on the slight dissociation of $Co(CNS)_4^{--}$ in acetone, since it is obvious that an excess of the thiocyanate does not have to be added for complete formation of the ion group.

Triangle Cross Section Parallel to Co^{++} – Acetone Side

This cross section corresponds to solutions with varying concentrations of cobalt and constant concentration of the thiocyanate. The results of absorption as a function of the cobalt concentration are listed in table 3 ([CNS] = 10^{-2} mole, thickness = 2 mm).

The results prove the existence of intermediate ion groups with especial clarity. Thus, in the 650 mμ region the intensity of the color rises at first as the $[Co^{++}]$ concentration is increased. If $Co(CNS)_4^{--}$ were the only stable

Table 3

Test No.	$Co^{++}:CNS^-$ ratio in mixture	Co^{++} concentration, moles	Log_e I_0/I At λ=650 mμ	At λ=570 mμ	At λ=500 mμ	Color or Co^{++} at λ=500 mμ	Absorption difference at λ = 500 mμ
1	2	3	4	5	6	7	8
1	1:6	$1.67 \cdot 10^{-3}$	0.55	0.22	0.01	–	–
2	1:5	$2 \cdot 10^{-3}$	0.66	0.30	0.03	–	–
3	1:4	$2.5 \cdot 10^{-3}$	0.68	0.40	0.05	–	–
4	1:3	$3.3 \cdot 10^{-3}$	0.66	0.44	0.15	0.06	0.09
5	1:2	$5 \cdot 10^{-3}$	0.55	0.48	0.16	0.06	0.10
6	1:1	10^{-2}	0.40	0.51	0.28	0.11	0.17
7	2:1	$2 \cdot 10^{-2}$	0.19	0.52	0.35	0.22	0.13
8	4:1	$4 \cdot 10^{-2}$	0.13	0.62	0.57	0.45	0.12

coordination compound in the system, an excess of cobalt (above what is required for the formation of $Co(CNS)_4^{--}$) would not cause any change in color (or some intensification of the color of Co^{++} itself). As the measurements made at λ = 650 m μ indicate, however, an excess of cobalt produces a quite noticeable weakening of the color. This weakening corresponds to reactions in which other coordination compounds with lower coordination numbers are formed:

$$3\ Co(CNS)_4^{--} + Co^{++} = 4\ Co(CNS)_3^-$$

$$2\ CO(CNS)_3^- + Co^{++} = 3\ Co(CNS)_2$$

In the 500 mμ region a solution of $Co(NO_3)_2$ in acetone is a strong absorber. Its own absorption is shown in Table 3, Col. 7, with the difference given in Col. 8. This difference rises up to a ratio of Co:CNS = 1:1, after which it begins to drop off. This testifies to the formation of the complex group $CoCNS^+$ and, apparently, to its further reaction with $Co(NO_3)_2$.

Groups with Low Numbers of Coordinated Thiocyanogen Ions

In analytical chemistry the blue group $Co(CNS)_4^{--}$ is of the greatest interest. But in order to characterize the reaction, groups with a lesser number of thiocyanogen ions were also investigated somewhat more thoroughly. The results indicated that the color of the solutions corresponds, on the whole, to the characteristic cited above, that it is sometimes complicated by the formation of more complicated cation groups. We cite below some results of the investigation of absorption spectra of mixed solutions of cobalt and thiocyanate. The work was done with a spectrodensograph, which makes it possible to obtain more detailed data on the absorption spectra of solutions. The results indicate that mixtures of $Co(NO_3)_2$ and $Co(CNS)^+$ are not additive, i.e., a reaction also occurs between these compounds. Thus, a $Co(NO_3)_2$ solution has a slight maximum at λ = 530 mμ (Fig. 3, Curve 1). A 1:1 solution of Co^{++} and CNS^- is characterized by Curve 2 (Fig. 3) with a diffuse maximum at about 600 m μ. Yet the solution Co:CNS = 2:1 does not yield an intermediate curve, but the characteristic Curve 3 with a maximum at about 530 mμ (the curves are plotted for the same cobalt concentrations).

This complicated interaction must be due to the formation of coordination compounds with the solvent. We consider that the formation of the cation group $Co_2(CNS)^{3+}$ in a compound with the solvent is most likely. The formation of such more complex cation groups of other ions is confirmed by the electrochemical research of Sillen and others,[8].

The properties of the spectra are considerably simpler in acid solutions. In Fig. 4 (Curves 1, 2, and 3) for instance, we give the data for the same

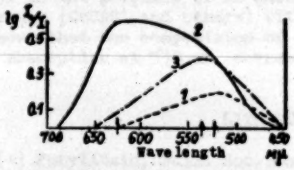

Fig. 3.
I-Co^{++} in acetone; 2-1:1 mixture of Co^{++} and CNS^- in acetone; 3-2:1 mixture of Co^{++} and CNS^- in acetone.

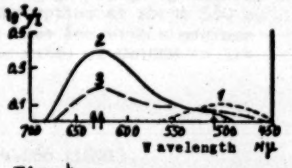

Fig. 4.
Co^{++} in acetone in the presence of a 0.1 molar solution of $HClO_4$; 2-a 1:1 mixture of Co^{++} and CNS^- in acetone in the presence of a 0.1 molar solution of $HClO_4$; 3-a 2:1 mixture of Co^{++} and CNS^- in acetone in the presence of a 0.1 molar solution of $HClO_4$.

solutions in the presence of 0.1 mole of $HClO_4$. Here addivitity generally prevails. The $HClO_4$ diminishes the dissociation of the HCNS, however, weakening the color of solutions of the group throughout the spectrum.

The $CoCNS^+ - Co(CNS)_4^{--}$ Groups

(Right-hand Side of the Triangle of Fig. 1)

The addition of the first thiocyanogen ion is followed by the formation of a number of other groups, which have an absorption maximum at about $\lambda = 630$ mμ. The absorption spectra of solutions of $Co(CNS)_2$ and of its mixtures with alkaline thiocyanates have been described in the literature, and therefore we shall not deal with their spectral characteristics here. The intensity of the color in the spectrum region around 630 mμ increases in such a way that, as a rule, the addition of each thiocyanogen ion (up to four, inclusive) causes an almost identical increase in the molar coefficient of extinction.

The literature data on ion transfer [3] of cobalt chloride in the presence of an excess of HCl or $CaCl_2$, as well as our experiments on cobalt ion transfer in the presence of thiocyanogen ions in acetone and mixtures of the latter with water (50% and 75%) and acidulated aqueous solutions confirm the formation of a complex blue anion.

SUMMARY

The formations of complex cobalt-thiocyanogen ions were studied by

the method of physicochemical analysis of the system consisting of a cobalt ion, a thiocyanogen ion, and a solvent (acetone). The extinction of solutions in various regions of the spectrum was studied as a property of the system.

2. Plotting the properties shows a maximum for various compositions, depending upon the wavelength at which absorption is measured. This phenomenon is explained by the general characteristic of step-by-step equilibrium. Formation of a number of steps was confirmed by investigation of various characteristic cross sections of the equilibrium triangle.

3. In the presence of an excess of cobalt we get slightly colored cation groups ($CoCNS^+$ and others) with maximum absorption at about 530 mμ. It was shown that the composition of the complex blue ion with a maximum spectral absorption at 530 mμ corresponds to the ratio of Co:CNS = 1:4.

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COMPOSITION AND INSTABILITY CONSTANT OF THE COMPLEX LEAD IODIDE ION

I. A. Korshunov and V. A. Osipova

Chair of Inorganic Chemistry, Gorky State University

When lead ions are reacted with an excess of iodine ions in solution, a reaction takes place, accompanied by the formation of complex anions that contain lead.

In most cases a coordination compound of iodine and lead in solutions is assigned two formulas: PbI_3^- and PbI_4^{--} [1] on the assumption that the formula for the crystalline structure of the complex ion group is preserved in the solution as well. This assumption is only partly justified. Equilibrium can be established in a solution between ion groups that have differing compositions, the concentration of one structure or another being determined by the concentration of the complex-ion constituent. Lanford and Kiehl [2] investigated the solubility of lead iodide in solutions of potassium iodide up to concentrations of 0.4N of the latter. They found, on the basis of their experimental data, that at these concentrations of potassium iodide two lead ion groups exist side by side in the solution.

But at low concentrations of potassium iodide, the percentage of the PbI_4^{--} ion group is low, the ion group poorer in iodine predominating. On the other hand, when the percentage of potassium iodide in the solution is 0.3-0.4N, the concentration of the PbI_3^- complex ion is negligibly small, practically all the lead existing in solution as a complex anion whose formula is PbI_4^{--}. Other authors likewise corroborate this fact. Korenman [3], for example, analyzing the data obtained by Golovaty [4] on the solubility of lead iodide in potassium iodide in concentrations up to 0.34N, comes to the conclusion that the PbI_3^- complex ion predominates in the above-mentioned solutions.

In a paper by one of the present authors together with Malyugina and Shchennikova [5], the polarographic method of analysis was employed to determine the composition of the group ion of lead iodide, it being shown that in solutions of potassium iodide ranging in concentration of the latter from 0.8 to 2.0M, a complex ion PbI_4^{--} is formed, with an instability constant of about 10^{-7}. According to Korenman's computations [3], this value lies between $1.87 \cdot 10^{-6}$ and $6.9 \cdot 10^{-9}$, whereas American authors give its value as $2.2 \cdot 10^{-9}$.

To get more precise values for the latter figure, we undertook a special investigation in which the method of measuring the e.m.f. of the concentration element was used to determine the composition and instability constant of the complex lead iodide ion.

EXPERIMENTAL

The concentration element was assembled as follows for these measurements:

$$Pb \;\Big|\; \begin{matrix} Pb^{++} \text{ conc.} \\ c_1 \end{matrix} \;\Big\|\; \begin{matrix} \text{Saturated} \\ \text{solution} \\ \text{of } KNO_3 \end{matrix} \;\Big\|\; Pb^{++} \;\; \begin{matrix} \text{in KI solution} \\ \text{concentrated } c_2 \end{matrix} \;\Big|\; Pb$$

in which the e.m.f. is generated by the leveling out of the concentrations of lead ions. Two electrodes of metallic lead, cast in rod form and terminated at their upper ends by glass tubes, were lowered to the bottom of two solutions of lead nitrate. A freshly prepared solution of potassium iodide was added to one of these solutions in varying amounts. The two vessels with lead electrodes were connected together, via intermediate solutions of the same composition, by an agar-agar bridge with a saturated solution of potassium nitrate to lower the diffusion potential difference.

The effect of the initial concentrations of lead nitrate and of the introduction of the electrolytic bridge upon the reproducibility and agreement of the end results was investigated in a series of tests.

It was found that the experimental results were unaffected by the foregoing factors if the concentration of the initial solutions of lead nitrate into which the lead electrodes were plunged did not exceed 0.01 mole/liter.

The surfaces of the lead electrodes were carefully cleaned with a steel knife before every measurement. After the potassium-iodide solution had been added to one of the lead-nitrate solutions, the container with the electrode, together with the whole electrolytic cell was kept in a thermostat until the e.m.f. remained constant, which usually required 5-6 hours.

The e.m.f. was measured at the following temperatures: 0, 25, 30, and 35° ± 0.1. We used a potentiometer that could measure e.m.f. to the nearest millivolt in our measurements.

Experimental Results

We used the equation for the magnitude of the e.m.f. of a concentration element:

$$E = \frac{RT}{nF} \ln \frac{[Pb^{++}]}{[x]} \quad , \qquad (1)$$

where x = the sought-for concentration of lead ions in the complex solution, and $[Pb^{++}]$ = the activity of the lead ions in the lead-nitrate solution, to calculate the concentration of lead ions in the solution of the complex iodide.

We took $[Pb^{++}]$ to be equal to the concentration of lead ions, as extremely dilute solutions were used in our research.

The results were plotted on co-ordinate paper: activity of the potassium iodide solution vs. concentration of lead ions.

Table 1

Concentration of Lead Ions in Solutions of Potassium Iodide at Various Temperatures

Activity of KI solution	Pb^{++} Concentration			
	0°	25°	30°	35°
0.9	$3 \cdot 10^{-9}$	$1 \cdot 10^{-8}$	$5 \cdot 10^{-8}$	$4.5 \cdot 10^{-7}$
1.17	$8 \cdot 10^{-10}$	$5 \cdot 10^{-9}$	$9.5 \cdot 10^{-9}$	$9.0 \cdot 10^{-8}$
1.35	$5 \cdot 10^{-10}$	$2 \cdot 10^{-9}$	$6.5 \cdot 10^{-9}$	$5.5 \cdot 10^{-8}$
1.62	$2 \cdot 10^{-10}$	$7.5 \cdot 10^{-10}$	$2.5 \cdot 10^{-9}$	$1.5 \cdot 10^{-8}$
2.00	$9.5 \cdot 10^{-11}$	$5.0 \cdot 10^{-10}$	$1.0 \cdot 10^{-9}$	$9.0 \cdot 10^{-9}$
2.20	$8.0 \cdot 10^{-11}$	$3.0 \cdot 10^{-10}$	$8.5 \cdot 10^{-10}$	$7.5 \cdot 10^{-9}$
2.90	$6.0 \cdot 10^{-11}$	$0.19 \cdot 10^{-10}$	$6.0 \cdot 10^{-10}$	$5.0 \cdot 10^{-9}$

Using this graph, we constructed a table of the solubility of lead ions in solutions of potassium iodide (Table 1).

The instability constants of the reactions were computed from Table 1:

$$PbI_3^- \rightleftharpoons Pb^{++} + 3I^- \quad k_1 = \frac{[Pb^{++}][I^-]^3}{[PbI_3^-]}$$

$$PbI_4^{--} \rightleftharpoons Pb^{++} + 4I^- \quad k_2 = \frac{[Pb^{++}][I^-]^4}{[PbI_4^{--}]}$$

The results are listed in Table 2. The figures given in Table 2 for the values of k_1 and k_2 for various concentrations of potassium iodide indicate the high constancy of the individual values of the second constant, viz.: k_2.

This enables us to assert that the principal complex ion formed in solutions of potassium iodide at concentrations of 1N and above is PbI_4^{--}.

Table 2

Instability Constant of the Lead Iodide Complex Ion at Various Temperatures

Activity of KI	Temperature							
	0°		25°		30°		35°	
	$k_1 \cdot 10^7$	$k_2 \cdot 10^7$	$k_1 \cdot 10^7$	$k_2 \cdot 10^7$	$k_1 \cdot 10^5$	$k_2 \cdot 10^5$	$k_1 \cdot 10^5$	$k_2 \cdot 10^5$
0.90	2.19	1.97	7.30	6.56	3.65	3.25	3.28	2.90
1.17	1.28	1.50	8.00	–	1.62	1.71	1.44	1.62
1.35	1.23	1.67	4.80	6.40	1.51	1.92	1.42	1.76
1.62	0.85	1.38	3.00	5.00	10.00	1.67	0.60	1.00
2.00	0.76	1.52	4.00	8.00	8.00	1.60	0.72	1.44
2.20	0.85	1.87	3.10	7.00	9.10	2.00	0.79	1.75
2.90	1.46	—	2.19	6.34	1.49	3.28	1.24	3.60
Average....	—	$1.60 \cdot 10^{-7}$	–	$6.30 \cdot 10^{-7}$	—	$2.3 \cdot 10^{-5}$	–	$2.0 \cdot 10^{-5}$

The numerical value found by us for the constant of instability of the complex lead-iodide anion confirms the figure found by the polarographic measurements and computed by Korenman from the solubility.

The value given by the American authors is considerably smaller.

To find the heat of reaction of complex formation we made use of the van't Hoff isochore equation. To do this the experimental values were plotted with $\log k_2$ — $1/T$, from which we estimated the heat of reaction of complex-ion formation as of the order of 59,000 calories per mole of the complex ion formed.

SUMMARY

1. The concentrations of lead ions in solutions of potassium iodide of various compositions at various temperatures were found from measurements of the e.m.f. of the concentration element.

2. It was found that in concentrated solutions of potassium iodide of 1N and higher a PbI_4^{--} complex anion is formed, with a constant of instability of the order of $5 \cdot 10^{-7}$ at room temperature.

3. The heat of formation of the complex anion was determined from the variations of the instability constant with temperature to be about 59,000 cal/mole.

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COMPOSITION AND INSTABILITY CONSTANT OF THE COMPLEX MERCURY THIOCYANATE ION

I. A. Korshunov and M. K. Shchennikova

Scientific-Research Institute of Chemistry,
Gorky State University

When potassium thiocyanate is introduced into a solution containing ions of bivalent mercury, a complex ion is formed, and the potential of the mercury drop electrode is displaced into the region of negative values. The same process occurs when the ions of univalent mercury react with potassium thiocyanate. This reaction is accompanied by a transformation of the univalent mercury to the bivalent form, half of the mercury separating out in metallic form, most probably in accordance with the following equation:

$$Hg_2^{\cdot\cdot} + 4CNS' \rightleftharpoons [Hg(CNS)_4]'' + Hg. \qquad (1)$$

In accordance with our measurements, the variation of the potential of the mercury drop electrode, $\pi_{1/2}$, with the concentration of the thiocyanate ion [CNS]' is described by the equation:

$$\pi_{1/2} = -0.152 - 0.125 \lg [CNS'], \qquad (2)$$

when the concentration of the potassium thiocyanate varies from 0.2 to 1.2N.

Whence:
$$\frac{d\pi_{1/2}}{d \lg[CNS']} = -0.125, \qquad (3)$$

which agrees rather well with the theoretical value of 0.116 for coordination number 4.

Thus, the $[Hg(CNS)_4]''$ complex anion of bivalent mercury exists at the above-mentioned concentrations of potassium thiocyanate.

To compute the instability constants from the polarographic changes we have to know the half-wave potential for the reduction of the ions of bivalent mercury when no complex ion groups are formed.

In our previous paper [1] it was shown that in solutions of potassium iodide bivalent mercury forms a stable coordination compound, $K_2[HgI_4]$, with the coordination number 4. The existence of such a coordination compound is corroborated by Remi [2], Lanford and Kiehl [3], and Grinberg [4].

The constant of instability for the reaction:

$$HgI_4^{--} \rightleftharpoons Hg^{++} + 4I, \qquad (4)$$

is $k_c = 5 \cdot 10^{-31}$, according to the data cited by the last of the authors cited. Using this figure, we computed the value of the half-wave potential for bivalent mercury in a 0.1N solution of potassium nitrate when no coordination compound is formed, since the experimental determination of this figure is difficult owing to the reduction of bivalent mercury by the metallic mercury of the electrode, in accordance with the reaction:

$$Hg^{++} + Hg \rightleftharpoons Hg_2^{++} . \qquad (5)$$

Computations using the equation for the potential displacement of the mercury drop electrode in the formation of complex ions

$$(\pi_{1/2})_k - (\pi_{1/2})_g = \frac{RT}{nF} \ln k_c - P \frac{RT}{nF} \ln a_{KI} \qquad (6)$$

resulted in the value $\pi_{1/2} = \pm 0.387$ V with respect to the saturated calomel electrode.

Using this figure, we computed the constant of instability of the complex ion of bivalent mercury and thiocyanogen, finding it to be $5 \cdot 10^{-20}$ at 18°. This latter value agrees fairly well with the value of $1 \cdot 10^{-22}$ cited by Grinberg [4]. It is possible that this agreement would be somewhat better if allowance were made for the coefficients of activity of potassium thiocyanate.

SUMMARY

1. The reduction of bi- and trivalent mercury in the presence of potassium thiocyanate was investigated.

2. The formula for the thiocyanate coordination compound of bivalent mercury $[Hg(CNS)_4]^{--}$ was established, and its instability constant: $K_c = 5 \cdot 10^{-20}$, was determined.

3. The half-wave potential of the reduction of the ion of bivalent mercury was computed from a 0.1 N solution of potassium nitrate as +0.387 volt.

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THE PHYSICOCHEMICAL ANALYSIS OF THE SYSTEMS FORMED BY DIPHENYLAMINE WITH PHENYL AND ALLYL ISOTHIOCYANATES

O. A. Osipov and N. A. Trifonov

V. M. Molotov Laboratory of Physical and Colloid Chemistry of the Rostov-on-Don State University

The systems mentioned in the title were investigated by us to ascertain the behavior toward the mustard oils of diphenylamine, which, on the one hand, as a secondary amine, ought to react with them to form substituted thiourea, [1,2], and, on the other, possesses greatly diminished basic properties, owing to the presence of two phenyl groups in its molecule.

MATERIALS AND METHODS

The diphenylamine was twice recrystallized from ligroin and freed of traces of the solvent in a vacuum exsiccator; m.p. 53.8°. The phenyl isothiocyanate, after drying over metallic sodium, was distilled at 218-218.5°, and then at reduced pressure; d_4^{25} 1.1282.

The allyl isothiocyanate, dried over calcium chloride, was distilled at 150-151°, and then in vacuum; d_4^{20} 1.0178.

The solution concentrations are expressed in molecular percentages in all cases.

The visual method of observing the appearance of the initial crystals and the disappearance of the last crystals from the solutions, which has been described more than once, was employed to determine the system's melting points. A mixture of ice and NaCl was used as the freezing mixture down to temperatures of -20°; below -20° we used a mixture of ice and $CaCl_2 \cdot 6H_2O$. Flow observations of the solution were made with the Ostwald-Luther viscosimeter, closed type.

Surface tension was determined by the Kantor method [3] as modified by P.A.Rebinder [4], with a number of auxiliary devices as suggested by one of the present authors,[5,6]. The manometer was attached exactly vertically against a ground-glass background. Readings were made with a microcathetometer. A thermometer, graduated to 0.1°, was placed between the arms of the manometer to facilitate temperature corrections of the latter's readings.

We used a large oil thermostat, equipped with a thermoregulator, that made it possible to keep the temperature constant within ± 0.1°, in making our measurements.

Phenyl Isothiocyanate – Diphenylamine System

This system is not described in the literature, not one of its physical properties being mentioned. We investigated its fusibility, viscosity, and surface tension.

The results of our fusibility measurements are given in Table 1 and Fig. 1.

Table 1

Fusibility of the Phenyl Isothiocyanate – Diphenylamine System

Solution No.	Mol.% of $(C_6H_5)_2NH$	Melting point, °.	Solution No.	Mol.% of $(C_6H_5)_2NH$	Melting point, °
1	0.00	-21.8°	8	45.00	+16.3
2	3.00	-24.0	9	50.00	+20.9
3	5.00	-25.2	10	55.00	+25.8
4	9.10	-28.4	11	60.00	+29.9
5	12.50	-23.0	12	80.00	+43.5
6	20.00	-12.0	13	100.00	+53.8
7	40.00	+11.4			

As is seen in Fig. 1, the fusibility curve consists of two branches: the phenyl isothiocyanate branch is almost a straight line, whereas the diphenylamine branch is concave downward toward the composition axis. The eutectic is at a temperature of -28.4° and a composition of 90.9 mol.% of the isothiocyanate.

Table 2

Viscosity of the Phenyl Isothiocyanate – Diphenylamine System

Solution No.	Mol.% of $(C_6H_5)_2NH$	Viscosity centipoises
1	0.00	0.92
2	20.00	1.13
3	40.00	1.53
4	45.00	1.65
5	50.00	1.81
6	55.00	2.02
7	60.00	2.25
8	80.00	3.29

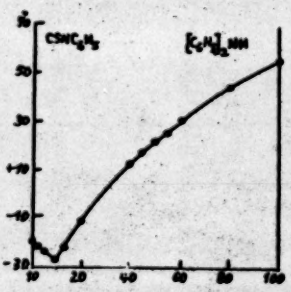

Fig. 1. Fusibility curve of the phenyl isothiocyanate – diphenylamine system.

Hence, the fusibility curve of the system indicates the absence of any chemical interaction between phenyl isothiocyanate and diphenylamine.

Table 2 and Fig. 2 give the values of the system's viscosity at 50°. The viscosity isotherm (Fig. 2) is a continuous curve, concave upward. According to Dunstan's classification [7], an isotherm of this sort is typical of systems containing chemically associated liquids that do not interact.

Surface temperature was measured at 50 and 75°.

The results of measurement are given in Table 3 and Fig. 3.

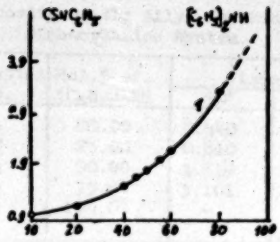

Fig. 2. Viscosity of the Phenyl Isothiocyanate – Diphenylamine system.

1-$\eta_{50°}$

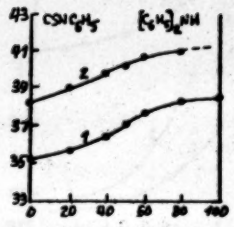

Fig. 3. Surface tension of the phenyl isothiocyanate-diphenylamine system.

1-$\sigma_{75°}$; 2-$\sigma_{50°}$

The isotherms for the system's surface tension at the two temperatures each consist of branches concave toward the amine end and convex toward the mustard oil end, the smooth inflection point occurring in the region of 50 mol.% of each of the two components. The form of this system's surface-tension isotherm classes it among the systems containing chemically noninteracting associated liquids, as well as among the irrational systems [8].

As we have already said, however, the fusibility curve and the viscosity isotherm do not furnish direct information on the chemical compounds in the system.

Table 3

Surface Tension of the Phenyl Isothiocyanate – Diphenylamine System

Solution No.	Mol.% of $(C_6H_5)_2NH$	Surface tension	
		50°	75°
1	0.00	38.24	35.20
2	20.00	39.08	35.84
3	40.00	39.82	36.39
4	50.00	40.42	37.01
5	60.00	40.64	37.64
6	80.00	40.99	38.28
7	100	–	38.67

It must therefore be considered that, judging by the form of its surface-tension isotherms, the phenyl isothiocyanate – diphenylamine system must be classed with the systems containing chemically noninteracting associated liquids.

Allyl Isothiocyanate–Diphenylamine System

The fusibility curve of the system, plotted by one of the present authors, disclosed no chemical interaction between the components.

The data of the viscosimetric study of the system at 50 and 75°, given in Table 4 and Fig. 4, likewise testify to the absence of chemical action in the system. The curve of the temperature coefficient of viscosity, γ, plotted

Table 4
Viscosity of the Allyl Isothiocyanate-Diphenylamine System

Solution No.	Mol.% of $(C_6H_5)_2NH$	Viscosity 50°	Viscosity 75°
1	00.00	0.540	0.455
2	25.00	0.810	0.540
3	50.00	1.319	0.797
4	75.00	3.101	1.510
5	100.00	–	3.040

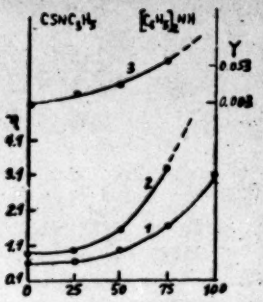

Fig. 4. Viscosity of the Allyl Isothiocyanate – Diphenylamine system.

1-$\eta_{75°}$; 2-$\eta_{50°}$; 3-$\gamma_{50-75°}$

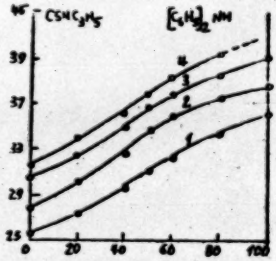

Fig. 5. Surface tension of the allyl isothiocyanate – diphenylamine system

1-$\sigma_{100°}$; 2-$\sigma_{75°}$; 3-$\sigma_{55°}$; 4-$\sigma_{70°}$

Table 5

Surface Tension of the Allyl Isothiocyanate – Diphenylamine System

Solution No.	Mol.% of $(C_6H_5)_2NH$	Surface tension 40°	55°	75°	100°
1	00.00	31.81	30.44	27.86	25.76
2	20.00	34.10	32.53	30.51	27.42
3	40.00	36.34	34.88	32.62	29.55
4	50.00	37.83	36.44	34.59	30.76
5	60.00	39.24	37.82	35.84	32.23
6	80.00	41.20	39.56	37.17	34.21
7	100.00	–	41.10	38.67	36.26

at the top of Fig. 4, is similar in form to the isotherms for the same property.

Preliminary measurements of the system's surface tension, made by one of the present authors together with A.N.Melnikova [10], yielded isotherms that were concave downward at the amine end and concave upward at the mustard oil end.

Our detailed investigations of the σ (c) over a wide temperature range confirms the preliminary data of A.N.Melnikova. The results of the measurement of surface tension at 40, 55, 75 and 100° are given in Table 5 and Fig. 5. The σ (c) isotherms are similar to those for the preceding system.

Thus, it may be stated as a fact that diphenylamine does not react with

mustard oils, thus differing from the behavior of such amines as methyl- and ethylaniline.

In this respect, therefore, it is like the tertiary amines, such as dimethyl-or diethylaniline, which do not enter into chemical reaction with these isothiocyanates.

SUMMARY

1. The fusibility, viscosity, and surface tension of the phenyl isothiocyanate – diphenylamine system were investigated.

2. The viscosity and surface tension of the allyl isothiocyanate – diphenylamine system were investigated.

3. It was established that diphenylamine does not enter into chemical reaction with these mustard oils.

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THE RATE OF FORMATION OF TETRAFLUOBORIC ACID IN MIXTURES OF HYDROFLUORIC AND BORIC ACIDS. I.

I. G. Ryss and M. M. Slutzkaya

Dnepropetrovsk Metallurgical Institute, Laboratory of General Chemistry

The data in the literature on the rate of formation of HBF_4 are as scanty and inaccurate as the data on the other properties of HBF_4 and the BF_4' ion.

The general investigations of the reaction velocity and equilibrium of hydrofluoric and boric acids made by one of the prominent representatives of classical physical chemistry and the author of a well-known handbook of inorganic chemistry, R. Abegg and his associates [1] did not yield precise conclusions. Abegg, Fox and Herz found that the electrical conductivity of mixtures of HF and H_3BO_3 reaches a constant value immediately after the components are mixed, which indicates that the reaction is instantaneous. From the nature of the "equivalent conductivity" of HF (computed for its overall percentage without allowing for the binding of HF in fluoborates) with dilution and with the $\frac{H_3BO_3}{HF}$ ratio, they concluded that one mole of a strong monobasic acid, i.e., HBF_4, as they had expected, was formed from 4 moles of HF. These authors found that the alkalimetric titer of the mixture declined with time. The inaccuracy of the method they used led them to the conclusion that in concentrated solutions one mole of H_3BO_3 combined with 4-5 moles of HF, and in dilute solutions with 9.6 moles of HF. From the acidity of the solutions, titrated against phenolphthalein, they found that 4 HF yielded 1 mole of a strong monobasic acid, contrary to the conclusion cited above. It is curious that whereas the titer was halved during the course of eight hours, the solution's conductivity remained practically unchanged. The rate of decrease of the titer at 26° corresponded to the course of a reaction that was nearly bimolecular. The mechanism of this reaction was not established by the authors; they did not even suggest that the drop in the titer was linked to the formation of BF'.

Travers and Malaprade [2] supposed that HF and H_3BO_3 react together instantaneously in aqueous solution, forming an acid that is easily decomposed by dilute alkalies and is slowly transformed (up to a certain condition of equilibrium) into HBF_4. They published only a few figures characterizing the variation of decrease in titer with time in a single mixture, containing 0.48 mole of HF and 0.12 mole of H_3BO_3 per liter of solution, at some unknown temperature.

A series of preliminary experiments undertaken by us showed that all the acidity can be titrated back immediately after dilute solutions of HF and H_3BO_3

at room temperature are mixed together; this can be followed very easily if the hydrofluoric acid is added to an excess of boric acid. Therefore, the formation of $BF_4^'$, which causes a reduction in the titrated acidity of the mixture, takes some time. The rate of formation of $BF_4^'$ may be computed from the loss of alkalimetric acidity as a function of time.

The formation of $BF_4^'$ is probably the result of a number of successive and, possibly, parallel reactions, which must make the kinetics of the process extremely complicated; in view of this we confined our efforts to obtaining data on the formal kinetics of the process, enabling us to judge the effect of concentration and temperature upon the rate of formation of the $BF_4^'$ in order to be able to make a prognosis as to the duration of the process when it is employed in analytical chemistry, synthetic procedures, etc.

Although deciphering the process mechanism was not part of our research goal, owing to its probable complexity, we desired to get some qualitative data to corroborate the intermediate formation of hydroxyfluoboric acid, which might elucidate the change in the $\frac{HF}{H_3BO_3}$ molecular ratio.

EXPERIMENTAL

The principal experiments were made at 30.05°. The solutions of HF and H_3BO_3 were kept in a thermostat for an hour. Then a definite volume of HF solution, measured in a pipette, was quickly added to the H_3BO_3 solution, with constant stirring. Samples of the mixture, taken at fixed intervals of time, were placed in an ice-chilled solution of sodium hydroxide, the slight excess of which was titrated back with a 0.1N solution of HCl after the addition of invert sugar and phenolphthalein.[1]

The containers and pipettes were covered with an even coating of paraffin.

The following notation may be used:

V_{al}, N_{al}, V_{ac}, and N_{ac} – volume (in ml) and normality of titrated solutions of NaOH and HCl.

q – molar ratio $\frac{HF}{H_3BO_3}$ in the initial mixture.

$\frac{M}{q}$ and M – initial molarity of H_3BO_3 and HF in the mixture.

φ – yield of HBF_4 (in parts of the stoichiometrically possible).[2]

w – volume of pipette sample for analysis (ml).

x – molarity of $BF_4^'$.

Since the formation of one mg-ion of $BF_4^'$, in accordance with the overall

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1) The reaction mixture was kept for 2 to 3 days at room temperature after conclusion of the test in order to determine the equilibrium state. The results have been published in one of our previous reports. [3]

2) With HF in excess, the stoichiometrically possible yield of $BF_4^'$ equals the quantity of H_3BO_3; with H_3BO_3 in excess, it equals one fourth the quantity of HF.

equation for the process: $4HF + H_3BO_3 = H^+ + BF_4^- + 3H_2O$, (1)

corresponds to a reduction of the overall acidity by 4 milliequivalents,

$$\frac{V_{al}N_{al} - V_{ac}N_{ac}}{w} = \frac{M}{q} + M - 4x. \qquad (2)$$

Whence, determining x and relating it to the stoichiometrically possible value, we find

$$\varphi = \frac{1+q}{4} - q\frac{V_{al}N_{al} - V_{ac}N_{ac}}{4Mw} \qquad (3)$$

for mixtures containing an excess of HF ($q > 4$), and:

$$\varphi = \frac{1+q}{q} - \frac{V_{al}N_{al} - V_{ac}N_{ac}}{Mw} \qquad (4)$$

for mixtures containing an excess of H_3BO_3 ($q < 4$).

Equations 3 and 4 are identical for $q = 4$.

In figures 1 - 5 the yield of HBF_4 is plotted as a function of the duration of the reaction at 30.05° for mixtures with various values of M and q. Duplicate tests were made for each mixture.

The possible error in the determination of φ may be evaluated from the well-known equation

$$\Delta\varphi = \sum \frac{\partial\varphi}{\partial x}\Delta y \qquad \text{where } y = \text{the quantity measured.}$$

Systematic errors for the given experiment (series of points) may result from errors in q, M, N_{al} and N_{ac}. The effect of changes in x is insignificant.

For $q > 4$, we find from Equation (3):

$$\left.\begin{aligned} \frac{\partial\varphi}{\partial q} &= \frac{1}{4} - \frac{V_{al}N_{al} - V_{ac}N_{ac}}{4Mw} = \frac{4\varphi - 1}{4q} \\ \frac{\partial\varphi}{\partial M} &= q\frac{V_{al}N_{al} - V_{ac}N_{ac}}{4M^2w} = \frac{1+q-4\varphi}{4M} \\ \frac{\partial\varphi}{\partial N_{al}} &= -q\frac{V_{al}}{4Mw} \\ \frac{\partial\varphi}{\partial N_{ac}} &= q\frac{V_{ac}}{4Mw} \end{aligned}\right\} \qquad (5)$$

For $q < 4$, we find from equation (4):

$$\left.\begin{aligned} \frac{\partial\varphi}{\partial q} &= -\frac{1}{q^2} \\ \frac{\partial\varphi}{\partial M} &= \frac{1+q-q\varphi}{Mq} \\ \frac{\partial\varphi}{\partial N_{al}} &= -\frac{V_{al}}{Mw}\ ;\ \frac{\partial\varphi}{\partial N_{ac}} = \frac{V_{ac}}{Mw} \end{aligned}\right\} \qquad (6)$$

If we assume that analytical errors are of the order of $\sim 0.2\%$, whereas errors in normality are $\sim 0.1\%$ i.e., $\frac{\Delta q}{q} = \frac{\Delta M}{M} = 2\cdot 10^{-3}$ and $\Delta N_{al} = \Delta N_{ac} = 10^{-4}$

and substitute the values for q, M, V , V_k and w applicable to the individual experiments, we get the following maximum values for $\Delta\varphi$:

for $q = 8$, $\Delta\varphi \cong 7\cdot 10^{-3}$;
for $q = 4$, $\Delta\varphi \cong 3\text{-}4\cdot 10^{-3}$;
for $q = 2$, $\Delta\varphi = 5\text{-}6\cdot 10^{-3}$,

i.e., the role of systematic errors is negligible in every case.

Random errors (fluctuations of the measured volumes of the alkalies and the reaction mixtures, titration errors) are of much greater significance.

From Equations (3) and (4) we find Equations (7) and (8), respectively, for $q > 4$ and $q < 4$:

$$\left.\begin{aligned} \frac{\partial\varphi}{\partial w} &= q\,\frac{V_{al}N_{al}\,V_{ac}N_{ac}}{4Mw^2} = \frac{1+q-4\varphi}{4w} \\ \frac{\partial\varphi}{\partial V_{al}} &= \frac{qN_{al}}{4Mw} \\ \frac{\partial\varphi}{\partial V_{ac}} &= \frac{qN_{ac}}{4Mw} \end{aligned}\right\} \qquad (7)$$

$$\left.\begin{aligned} \frac{\partial\varphi}{\partial w} &= \frac{V_{al}N_{al}-V_{ac}N_{ac}}{Mw^2} = \frac{1+q-q\varphi}{qw} \\ \frac{\partial\varphi}{\partial V_{al}} &= -\frac{N_{al}}{Mw} \\ \frac{\partial\varphi}{\partial V_{ac}} &= -\frac{N_{ac}}{Mw} \end{aligned}\right\} \qquad (8)$$

In all the experiments, $w \cong 10$ ml; $\Delta w \cong 0.04$ ml; $N_{ac} \cong N_{al} \cong 0.1$; hence,

$$\frac{\partial \varphi}{\partial V_{al}} = \frac{}{V_{ac}}.$$

The value of ΔV_{al} is governed by the volume of the pipette used; the value of ΔV_{ac} might be taken as equaling 0.05 to 0.1 ml, depending on the volume of the solution to be titrated and on whether an ordinary burette or a microburette is used.

The principal experimental conditions and the maximum[1] values of $\Delta\varphi$ for the assumed errors are listed in Table 1. The table also lists the values of attainable at room temperature.

Table 1

	q = 8		q = 4			q = 2		
Initial molarity of HF, M = ...	0.2681	0.1388	0.2681	0.1388	0.0788	0.2681	0.0788	0.0394
Equilibrium value of φ = ...	0.998	0.94-0.96	0.82 - 0.85	0.77 - 0.78	0.69	0.735	—	—
Kinetics traced up to $\varphi \approx$	0.9	0.8	0.8	0.65	0.4	0.7	0.4	0.2
$V_{al} \approx$	24	12.5	29	15	9	31	9	5.5
$\Delta V_{al} \approx$	0.05	0.05	0.06	0.05	0.05	0.07	0.05	0.05
$\Delta V_{ac} \approx$	0.1	0.05	0.1	0.05	0.05	0.1	0.05	0.05
$10^2 \frac{\partial \varphi}{\partial w} \Delta w$ = ...	0.9 - 0.5	0.9 - 0.6	0.5 - 0.2	0.5 - 0.2	0.5 - 0.3	0.6 - 0.3	0.6 - 0.4	0.6 - 0.5
$10^2 \cdot \frac{\partial \varphi}{\partial V_{ac}} \times (\Delta V_{al}+\Delta V_{ac})$=....	1.1	1.1	0.6	0.6	1.0	0.6	1.0	2.0
$10^2\Delta\varphi$ =....	2-1.6	2-1.7	1.1 - 0.8	1.1 - 0.8	1.5 - 1.3	1.2-0.9	1.6-1.4	2.6-2.5

Comparison of these values with the experimental data showns that in most cases $\Delta\varphi$ was below the maximum values listed in Table 1.

Fig. 1 shows the results of the tests, in which the initial molarity of HF remained constant. (0.2681), but the ratio HF/H_3BO_3 was varied. When there was not enough boric acid present (q = 8), the rate of formation of HBF_4 rises; when it is present in excess, i.e., when the concentration of boric acid is increased (q = 2), the rate of formation of HBF_4 is reduced; the drop in the reaction rate when the concentration of one of the reagents is raised clearly indicates the complicated nature of the chemical action involved.

The initial portion of the curves is shown on an enlarged scale in Fig. 2. It is evident that the initial value of $\frac{d\varphi}{dt}$ is hardly at all affected by q.

1) I.e., corresponding to the case where the effect of every error is in the same direction.

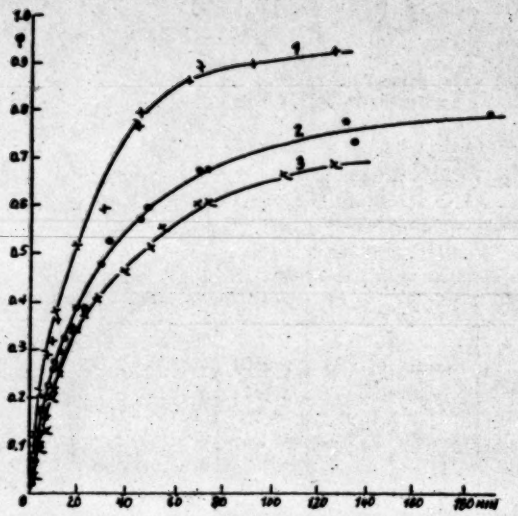

Fig. 1. HBF_4 yield (in parts of the stoichiometrically possible) as a function of the length of the test, for M = 0.2681

1) $\frac{HF}{H_3BO_3} = 8$; 2) $\frac{HF}{H_3BO_3} = 4$; 3) $\frac{HF}{H_3BO_3} = 2$.

Figs. 3 and 4 show the HBF_4 yield as a function of time for an initial molarity of HF that is about half what was used in the previous tests (0.1388 M); Fig. 5 gives the same function for M = 0.0788 and 0.0394. In these latter cases, a reduction of q for constant initial HF molarity diminishes $\frac{dq}{dt}$, but still less markedly than for M = 0.2686.

Comparison of the curves for the same $\frac{HF}{H_3BO_3}$ ratio, but for various concentrations, shows that the reaction velocity rises sharply when the overall concentration of the solution is increased.

The reaction time required to attain a given HBF_4 yield at different dilutions is given in Tables 2 and 3. The figures in parentheses are the values for the formal reaction order, computed from a comparison of the reaction time for the given concentration and for the next lower concentration (for constant q). The calculations were made in the well-known formula:

$$\left(\frac{M_1}{M_2}\right)^{n-1} = \frac{t_2}{t_1},$$

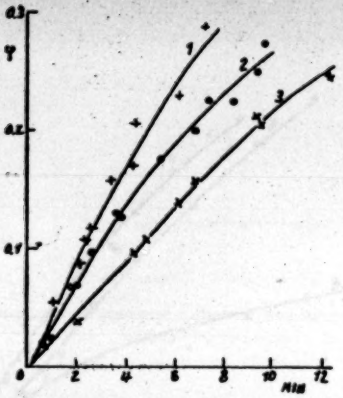

Fig. 2. Initial portions of the curves of Fig. 1.

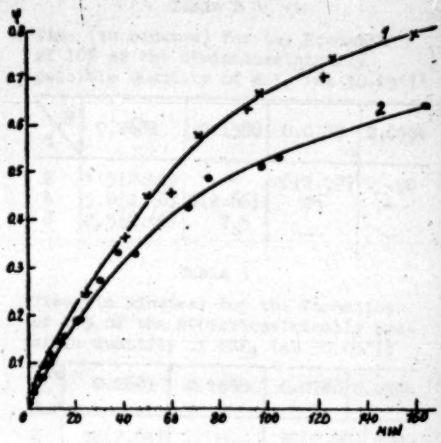

Fig. 3. HBF_4 yield (φ) as a function of the length of the test for M=0.1388
1) q = 8; 2) q = 4.

where n = the order of the reaction, and t_1 and t_2 are the lengths of time required to attain the same value of φ.

The formal order of the reaction in mixtures where q = 4 and q = 8 lies within the range 2.7-3. In mixtures with an excess of H_3BO_3 there is a tendency for the order of the reaction to decrease.

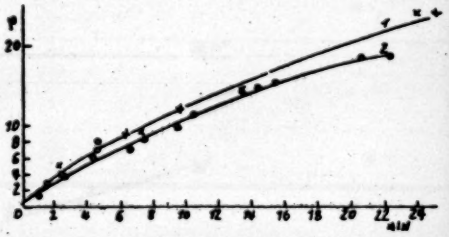

Fig. 4. Initial portions of the curves of Fig. 3.

The results given in Tables 2 and 3 might lead one to suppose that the formation of HBF_4 ought to be very rapid in concentrated hydrofluoric acid. In fact, when a weighed batch of crystalline boric acid is placed in 20% hydrofluoric acid (previously chilled to 10° to eliminate the influence of reaction heat), equilibrium was reached within 2-3 minutes.

The effect of temperature upon the reaction in which HBF_4 is formed, in a mixture with M = 0.0788 and q = 4, is illustrated in Fig. 6. Higher temperatures accelerate the reaction sharply, but they reduce the equilibrium HBF_4 yield markedly. As shown in another report [3], the change in the equilibrium yield of HBF_4 in these experiments corresponds to the temperature variation of BF_4^- hydrolysis previously discovered.

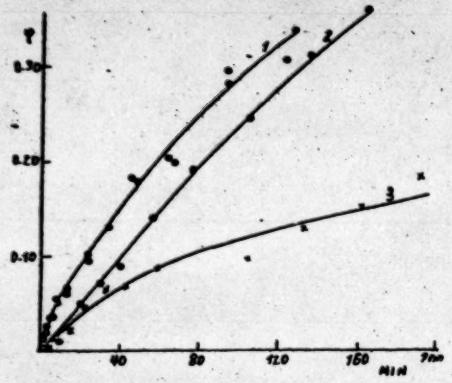

Fig. 5.
1) M = 0.0788; q = 4;
2) M = 0.0788, q = 2;
3) M = 0.0394, q = 2.

Table 2

Time (in minutes) for the Formation of 10% of the Stoichiometrically possible Quantity of HBF_4 (at 30.05°)[1]

q \ M	0.2681	0.1388	0.0788	0.0394
2	4.5(2.43)	–	26(2.79)	~90
4	3.0(2.66)	9(2.66)	23	–
8	2.5(2.66)	7.5	—	–

Table 3

Time (in minutes) for the Formation of 25% of the Stoichiometrically possible Quantity of HBF_4 (at 30.05°)[1]

q \ M	0.2681	0.1388	0.0788	0.0394
2	12(2.64)	–	90(2.58)	270
4	9(2.82)	30(2.84)	85	–
8	6.5(3.04)	25	–	–

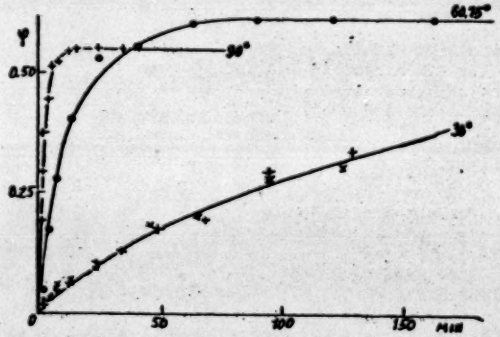

Fig. 6. Effect of Temperature upon the variation of HBF_4 yield with time (M = 0.0788; q = 4).

1) Reaction order in parentheses

SUMMARY

1. The rate of formation of HBF_4 at 30° was determined in mixtures of hydrofluoric and boric acids, at initial concentrations of HF ranging from 0.268 M to 0.0394 M, and at $\frac{HF}{H_3BO_3}$ ranging from 8 to 2.

The reaction rate rises slightly when the $\frac{HF}{H_3BO_3}$ ratio rises, and rises sharply as the solution concentration is increased. The formal order of the reaction is close to 2.7 - 3. In 20% HF the reaction is finished within 2-3 minutes.

2. Higher temperature sharply increases the rate of formation of HBF_4, at the same time lowering its equilibrium yield.

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[3] I. G. Ryss and M.M. Slutskaya, Reports of the USSR Acad. Sci., 57, 689 (1947).

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THE RATE OF FORMATION OF TETRAFLUOBORIC ACID IN MIXTURES OF HYDROFLUORIC AND BORIC ACIDS. II.

I. G. Ryss

Dnepropetrovsk Metallurgical Institute, Laboratory of General Chemistry

In the preceding report [1] we cited the results of the experimental study of the rate of formation of HBF_4 in mixtures of hydrofluoric and boric acids. Although it was not the object of that research to determine the mechanism of the reaction, the results obtained, when collated with facts previously known, enable us to make some preliminary conclusions in this respect as well.

In studying the equilibrium of the hydrolysis of BF_4^- [2] and the formation of tetrafluoboric acid [3], we demonstrated the existence of the following equilibrium:

$$BF_4^- + H_2O \rightleftarrows BF_3OH^- + HF, \qquad (1)$$

for which:

$$\Delta F_{298}^\circ = 3.57 \text{ Cal}; \quad \Delta S_{298} = -1.1 \ \frac{\text{Cal.}}{^\circ C} \text{ and } \Delta H = 3.25 \text{ cal.}$$

The possibility of the stable existence of BF_3OH^- was also proved by the synthesis[1] of KBF_3OH [4]. The BF_3OH^- ion differs from BF_4^- [5], which decomposes extremely rapidly in alkali, in that it is titrated to a fluoride by an alkali as well as to a borate (in the presence of invert sugar).

The BF_3OH^- ion should be looked upon as the anion of the strong hydroxy fluoboric acid or the hydrate of boron fluoride: $BF_3 \cdot 2H_2O = H_3O[BF_3OH]$.

These data enable us to comprehend the thermochemical data of Thomsen [6] which he himself could not explain. Thomsen found that when dilute[2] aqueous solutions of HF and H_3BO_3 are mixed together, the heat of reaction rises proportionally to the ratio $q = \frac{HF}{H_3BO_3}$ only up to $q = 3$.

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1) There is a typographical error in the paper describing the synthesis and the properties of KBF_3OH: when it is synthesized from a mixture with a ratio of $KHF_2 : H_3BO_3 = 1.98$, 10g of H_3BO_3 (and not 20 g, as erroneously stated on p. 328)) are added to 25 g of KHF_2.

2) 1/12 mole of H_3BO_3 in a solution with a water equivalent of 300 was mixed with a HF solution having a water equivalent of 900.

Q290 - a 291

$q = \frac{HF}{H_3BO_3}$	Heat of reaction per mole of H_3BO_3 (in cal)
1	4566
2	9300 = 2.4650
3	13734 = 3.4578 [1]
4	14739 = 4.3685
5	14568 = 6.2428

When q rises to 3, the rapid and strongly exothermic formation of $BF_3 \cdot 2H_2O$ is observed. Further increase of q tends to cause the formation of HBF_4, but this process is only slightly exothermic and takes some time.

In 1912 Mulert [8], measured the heat of solution of B_2O_3 in 3.65% HF, finding that a rapid and strongly exothermic process (29.64 Cal/mole of B_2O_3) was followed by a slow and slightly exothermic process. He observed a similar phenomenon when dissolving hydrous boric acid in HF.

Apparently, the rapid process is the formation of the hydroxyfluoboric acid, whereas the slow process is the conversion of the latter into tetrafluoboric acid. Travers and Malaprade [7], making a potentiometric study of the interaction between solutions of HF and H_3BO_3, found that an acid easily decomposed by dilute alkalies is formed instantaneously, thereafter being slowly transformed into tetrafluoboric acid. The fact that all the acidity can be titrated back immediately after the dilute solutions of HF and H_3BO_3 have been added [1] also confirms this point of view.

Let us now consider the kinetic behavior we have found from two standpoints: I) the immediate formation of HBF_4, and II) the intermediate formation of hydroxyfluoboric acid.

We shall use the following notation:

M = initial molarity of HF in the mixture;

q = molar ratio $\frac{HF}{H_3BO_3}$ in the mixture;

φ = yield of BF_4' in parts of the stoichiometrically possible;

x = molarity of the BF_4' formed.

I) Let us assume that the reaction in which BF_4' is formed takes place with the immediate participation of the boric acid and obeys the law of third-order reactions:

$$4HF + H_3BO_3 = HBF_4 + 3H_2O \qquad (2)$$

Variant A

$$M - 4x \quad \frac{M}{q} - x.$$

$$\frac{dx}{dt} = k(HF)^2(H_3BO_3) = k(M - 4x)^2\left(\frac{M}{q} - x\right) \qquad (3)$$

With an excess of HF

$$x = \frac{M}{q}\varphi \; . \qquad (4)$$

---

1) In volume 1, p.231, Thomsen cites Q=12.816 Cal for q = 3, i.e. he found a departure from proportionality even for lower values of the $HF:H_3BO_3$ ratio.

Substituting this value in Equation (3) and transposing, we get:

$$\frac{d\varphi}{dt} = kM^2(1-\varphi)\left(1-\frac{4\varphi}{q}\right)^2 . \qquad (5)$$

It is evident that in the initial stage of the reaction, i.e., for low values of :

$$\frac{d\varphi}{dt} \cong kM^2 \not{f}(q), \qquad (6)$$

which clearly contradicts the experimental findings.

When insufficient HF is present

$$x = \frac{M\varphi}{4} . \qquad (7)$$

Substituting this value in Equation (5), we find:

$$\frac{d\varphi}{dt} = 4kM^2\left(\frac{1}{q}-\frac{\varphi}{4}\right)(1-\varphi)^2, \qquad (8)$$

whence, in the initial stage of the reaction:

$$\frac{d\varphi}{dt} \cong \frac{4kM^2}{q} . \qquad (9)$$

Equation (9) is in sharp contradiction to experimental results, as the value of $\frac{d\varphi}{dt}$ falls as q diminishes, whereas Equation (9) requires that $\frac{d\varphi}{dt}$ increase.

Variant B:

$$\frac{dx}{dt} = k(HF)(H_3BO_3)^2 = k(M-4x)\left(\frac{M}{q}-x\right)^2 . \qquad (10)$$

For an excess of HF ($q > 4$), we find, similarly:

$$\frac{d\varphi}{dt} = k\frac{M^2}{q}(1-\varphi)^2\left(1-\frac{4\varphi}{q}\right) \cong \frac{kM^2}{q} ; \qquad (11)$$

and for an excess of H_3BO_3 ($q < 4$):

$$\frac{d\varphi}{dt} = 4M^2k(1-\varphi)\left(\frac{1}{q}-\frac{\varphi}{4}\right)^2 \cong \frac{4kM^2}{q^2} . \qquad (12)$$

Equation (11), and particularly Equation (12) contradict the experimental data (effect of changes in q!) and hence Variant B must likewise be rejected.

The inapplicability of Equation (I) can be simply proved by qualitative considerations for a transition from $q = 4$ to $q = 2$ for a constant M. In such cases the values of $\frac{d\varphi}{dt}$ are similarly related to the reaction velocity $\frac{dx}{dt}$.

According to the suggested equation, an increase in the concentration of the boric acid ought to increase the reaction rate (particularly in Variant B). But experiment shows that the reaction rate falls.

II) In accordance with the literature data cited above it is advisable to assume that for $q > 3$ the first stage of the reaction is a rapid process:

$$H_3BO_3 + 3HF = [BF_2OH]' + H^+ . \qquad (13)$$

$$M \quad \left(-\frac{3}{q}\right) \qquad M/q \qquad M/q$$

For the bimolecular reaction involving the formation of BF_4' to be conveyed by the equation for a third-order reaction it must be assumed that a rapidly established equilibrium persists in the solution:

$$BF_3OH' + H^+ \rightleftharpoons BF_3H_2O; \quad K_p = \frac{[BF_3OH'][H^+]}{[BF_3H_2O]} \qquad (14)$$

and that the process limiting the formation of BF_4' is governed by the equation:

$$BF_3H_2O + HF = BF_4' + H^+ + H_2O.\ ^1 \qquad (15)$$

The catalytic action of the hydrogen ions in the process of forming the BF_4' is quite understandable, since they also accelerate the reverse process: the hydrolysis of BF_4 [5].

As BF_3H_2O is a strong acid [2,3] and the dissociation of the HF is suppressed practically altogether, the concentration of hydrogen ions remains approximately constant throughout the reaction, equaling $\frac{M}{q}$. The lowering of the concentration of BF_3OH' due to the formation of BF_3H_2O may also be ignored.

The concentrations of the reagents are determined by the following equations:

$$\left.\begin{aligned} [BF_4'] &= x \\ [HF] &= M\frac{q-3}{q} - x \\ [H^+] &\approx \frac{M}{q} \\ [BF_3OH'] &\approx \frac{M}{q} - x \\ [BF_3H_2O] &= \frac{1}{K_p}[BF_3OH'][H^+] = \frac{1}{K_p}\left(\frac{M}{q} - x\right)\frac{M}{q} \end{aligned}\right\} \qquad (16)$$

whence the equation for the reaction rate is given by the expression:

$$\frac{dx}{dt} = k[BF_3H_2O][HF] = \frac{k}{K_p}\frac{M}{q}\left(\frac{M}{q} - x\right)\left(M\frac{q-3}{q} - x\right). \qquad (17)$$

After substituting $x = \frac{M}{q}\varphi$ and transposing, we get:

$$\frac{d\varphi}{dt} = \frac{k}{K_p} M^2 \frac{(q-3-\varphi)}{q^2}(1-\varphi). \qquad (18)$$

---

1) The reactivity of the inner sphere rises sharply during the transition from BF_4' to BF_3OH'. Possibly, BF_3H_2O is even more reactive owing to an increase in the part played by dipole bonds, with a probable shift from a tetrahedral configuration to a pyramidal one.

At the beginning of the reaction, i.e., for small values of φ:

$$\frac{d\varphi}{dt} = \frac{k}{K_p} M^2 \frac{q-3}{q^2} . \qquad (19)$$

Equation (19) expresses the experimentally observed sharp drop in the value of $\frac{d\varphi}{dt}$ with rising M, and the negligible increase in $\frac{d\varphi}{dt}$ with rising q, very well.[1]

To check the applicability of this equation, let us compare the experimental data for $\varphi = f(t)$ with the equation derived by integrating Equation 18:

$$\frac{4-q}{q^2} M^2 \frac{k}{K_p} t = \ln (q-3) + \ln \frac{1-\varphi}{q-3-\varphi} . \qquad (20)$$

Fig. 1 is a plot of our data for q = 8, with the co-ordinates t, $\log \frac{q-3-\varphi}{1-\varphi}$, in which Equation (20) undergoes linear anamorphosis. The experimental data lie fairly close to a straight line; only at $\varphi > 0.75$ is there a marked deviation, due, no doubt to the reversibility of the reaction.

The values of $\frac{k}{K_p}$ computed from the angular coefficients of the straight lines and the values of q and M are listed in Table 1, proving that these quantities also are sufficiently constant.

For q = 4, integration of Equation (18) yields the following expression:

$$\frac{M^2 k}{16 K_p} t = \frac{\varphi}{1-\varphi} . \qquad (21)$$

The experimental data for mixtures with q = 4 are plotted in Fig. 2 with the co-ordinates t, $\frac{\varphi}{1-\varphi}$;

The experimental data lie close to a straight line.[2]

The computed values of $\frac{k}{K_p}$ listed in Table 1 are close to those found earlier, which is a serious argument in favor of the correctness of the reaction equation we have assumed.

Table 1

Values of k/K_p in $l^2 \cdot mole^{-1} \cdot min^{-1}$

q \ M_0	0.2681	0.1388	0.0788
4	7.3	9.3	11
8	7.3	8.0	—

The drop in $\frac{k}{K_p}$ as the solution concentration rises is possibly related to a progressive departure from the laws of ideal solutions.

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1) As may be easily seen, the function $\frac{q-3}{q^2}$ has a maximum at q = 6 and thus undergoes little change between the values of 4 and 8 for q. As q grows from 4 to 8, $\frac{q-3}{q^2}$ increases from 0.0625 to 0.0782, or by 12.5%.

2) The systematic deviation at $\frac{\varphi}{1-\varphi} > 2$, i.e., $\varphi > 0.67$ is apparently due to the effect of the reverse reaction.

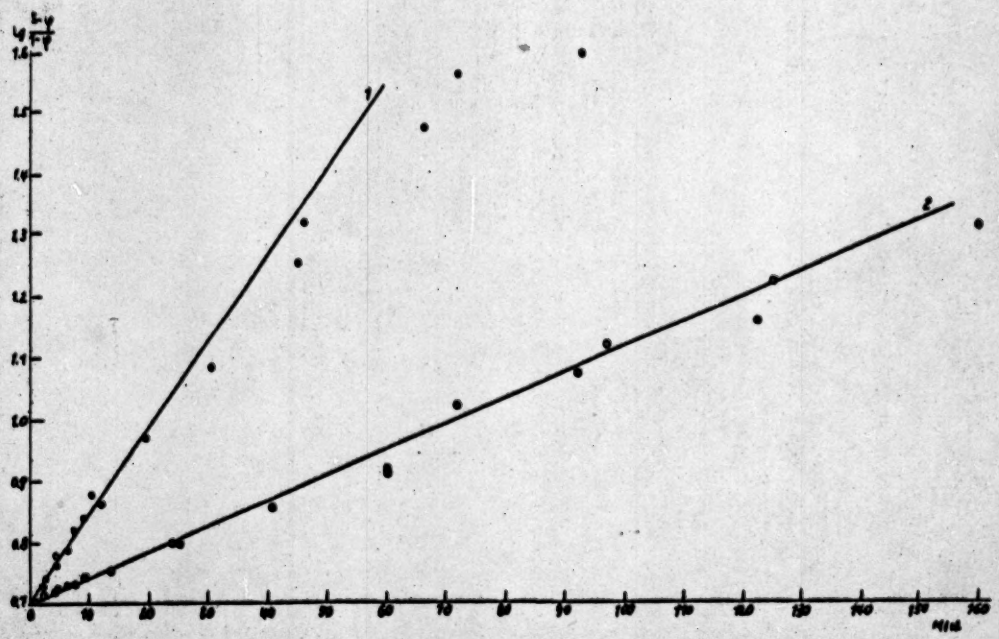

Figure 1

1-q =6; H =0.2681; 2-q =6; H =0.1366

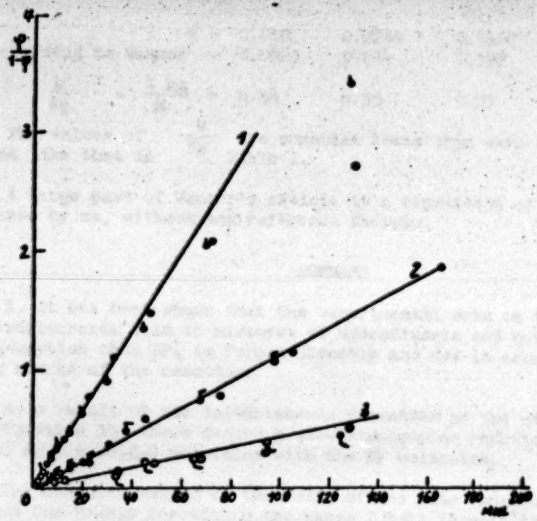

Fig. 2

1) q = 4; M = 0.2681; 2) q = 4; M = 0.1388; 3) q = 4; M = 0.0788.

Abegg, Fox, and Herz [9] noted a seemingly paradoxical fact: when HF is mixed with H_3BO_3, the electrical conductivity of the mixture is established instantaneously and undergoes practically no change with time, despite the considerable decrease in alkalimetric acidity. The reaction equation we have assumed makes it possible to explain these data as well; as the mobilities of the BF_3OH' and BF_4' must lie very close together, and as the degree of electrolytic dissociation of BF_3H_2O is high, while the dissociation of HF is suppressed, the course of the process described by Equation 15 cannot affect the solution's conductivity appreciably.

The adopted equation cannot be employed for solutions containing an excess of boric acid over the quantity needed for the formation of the BF_3H_2O, ($q < 3$), as an extremely sharp drop in the concentration of free HF ought to cause a pronounced decrease in the reaction rate. Experiment shows that a transition from q = 4 to q = 2 causes a negligible drop in the reaction rate. The experimental data available is insufficient for setting up even a hypothetical reaction equation.

Wamser [10] described the rate of formation of HBF_4 at 25° in three solutions for which q = 4. The equation assumed by him for the processes corresponds to our Equations (13) and (15), the overall HBF_3OH percentage being used in Equation (15). The rate constants K_1 computed by him for the bimolecular process (15) increase rapidly with the solution concentration. Recalculation of his data in terms of our equation yields the following results.

M =	0.052	0.2244	0.4420
K_1 according to Wamser =	0.0823	0.244	0.392
$\frac{k}{K_p} = \frac{4\,kg}{M}$ =	6.34	4.35	3.55

The values of $\frac{k}{K_p}$ are somewhat lower than ours at 30.05° and follow a trend like that in Table 1.

A large part of Wamser's article is a repetition of the papers previously published by us, without any reference thereto.

SUMMARY

1. It has been shown that the experimental data on the rate of formation of tetrafluoboric acid in mixtures of hydrofluoric and boric acids contradict the assumption that BF_4' is formed directly and are in accordance with the following course of the reaction:

As a result of the instantaneous formation of the strong hydroxyfluoboric acid (Equation 13) there occurs a slow bimolecular reaction of the undissociated portion of the BF_3H_2O molecules with the HF molecules.

The computed values of the ratio of the rate constant to the dissociation constant for BF_3H_2O lie within the range 7.3-11 $l^2 \cdot mole^{-1} \cdot min^{-1}$.

2. The adopted equation explains the results of measurements of the heat of solution of boric acid in hydrofluoric acid and measurements of the conductivity of such mixtures made by other authors.

3. The reaction mechanism should be a different one for mixtures in which $\frac{HF}{H_3BO_3} < 3$.

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KINETICS OF THE PROCESSES OF ROASTING, LEACHING, WASHING AND CEMENTATION

A. L. Rotinyan and B. V. Drozdov

Institute of the Nickel-Cobalt and Tin Industry, Leningrad

INTRODUCTION

In spite of the great importance of problems of reaction rates in roasting, leaching, washing, and cementation, no generalized laws governing the kinetics of these reactions have been established as yet. Only a few endeavors have been made to substantiate the applicability of Nernst's diffusion theory. In practice, we have been confined to purely empirical data, as Nernst's theory is inapplicable to hydrometallurgical processes, and the equations derived from it yield results that depart considerably from experiment.

The present paper investigates the general laws governing the kinetics of the processes of roasting, leaching, washing, and cementation. The formula derived agrees with numerous experiments performed by various authors.

The foundation underlying this work has been the conclusion reached by B.B.Drozov in his study of the cementation process.*

DEVELOPMENT OF THE BASIC FORMULA

In developing this formula we started with the condition of uniform distribution of the solid reacting component within the aggregate mass of solid particles. In actuality, the distribution of the solid component may vary considerably in individual grains, but this distribution is evened out when a large number of grains is taken.

Likewise, the diffusion rate varies not only in different particles, but in different directions within a single particle. Hence, we shall henceforth have to use as the diffusion rate and the coefficient of diffusion the mean values for material at a given stage of fineness.

We also assume that the reaction is formally a first-order one, taking place under isothermal conditions, and without secondary reactions or mechanical crushing of the grains.

Despite the marked differences in the chemical nature of the roasting, leaching, washing, and cementation reactions, their kinetics have much in common.

All the processes discussed are heterogeneous reactions that take place between solid particles and a gas (roasting) or a liquid (leaching, washing,

*Reported at the 2nd All-Union Conference on Electrochemistry (Kiev, 1948).

and cementation).

The distinguishing characteristic of the foregoing reactions is the gradual growth of a diffusion layer through which liquid or gaseous reagents pass in one direction, with the liquid or gaseous reaction products passing through it in the opposite direction.

As a rule, the reaction commences at the surface of the solid particle, penetrating into the interior of the grain as it proceeds, gradually forming a growing, porous, solid crust of reaction products or of inert unreacted material, or finally, of both together.

Thus, in the initial stage of the process, when the reaction occurs at the particle's surface, the kinetics are governed by the velocity of the chemical reaction itself. As the crust grows, its role in the reaction kinetics increases. There are three possible cases, depending on the structure and other peculiarities of the crust:

1. The crust is highly porous; when this is so, the overall velocity of the process is determined entirely by the chemical reactions themselves, as the rate of diffusion is many times the reaction rate. Despite the continuous increase in thickness of the crust, it exerts no effect upon the nature of the kinetics.

In this case, therefore, the usual first-order kinetics equation applies.

2. The crust has low porosity; in this case, the kinetics are, in general, limited by the rate of diffusion of the liquid or gaseous reagents through the porus crust into the reaction zone.

3. The crust is of average porosity; the diffusion and reaction rates are then commensurable.

The operations set forth in the title of this article are either performed at constant volume (agitation), or in a current of liquid or gas (percolation, most kinds of roasting).

Let us derive the kinetics equation for the processes that occur at constant volume. Our notation is as follows:

a = initial concentration of reagent.

x = concentration of the reagent that has already reacted at time t.

D = mean coefficient of diffusion of the reagent through the crust.

S = phase separation surface.

λ = thickness of crust.

v = volume of reagent.

ζ = reagent concentration at surface where reaction is occurring at given instant.

k = constant of first-order reaction rate.

μ = coefficient allowing for the transition from surface to volume concentration.

Let us consider the kinetics when the diffusion rate is commensurable with the reaction rate [1].

In this case, a stationary state sets in within an extremely short interval of time after the beginning of the reaction, which may be characterized by the following equation:

$$\frac{dc}{dt} = \frac{1}{\mu}\frac{dx}{dt} = k\zeta = \frac{D}{\lambda}[(a - x) - \mu\zeta]. \qquad (1)$$

The thickness of the crust does not remain constant, but grows continuously, and hence may be replaced by $\underline{x}$ on the basis of the following equation:

$$B = \frac{xv}{S\lambda}. \qquad (2)$$

Here $\underline{B}$ is the quantity of reagent that reacts per unit volume of the solid phase. When the useful constituents are evenly distributed throughout the material, $\underline{B}$ is a constant.

Combining (1) and (2), we get:

$$k\zeta = \frac{DSB}{xv}[(a - x) - \mu\zeta]. \qquad (3)$$

whence:

$$\zeta = \frac{DSB(a - x)}{kxv + DSB\mu} \qquad (4)$$

and

$$\frac{dx}{dt} = \frac{kDSB\mu(a - x)}{kxv + DSB\mu}. \qquad (5)$$

Integrating Equation (5) over the following boundary conditions:

$$t = 0; \quad x = 0 \qquad (6)$$

yields the equation:

$$\frac{1}{t}\ln\frac{a}{a - x} - \beta\frac{x}{t} = M, * \qquad (7)$$

in which:

$$\beta = \frac{vk}{kva + DSB\mu} \qquad (8)$$

and

$$M = \frac{kDSB\mu}{kva + DSB\mu}. \qquad (9)$$

Let us now examine the two boundary cases: a) when the diffusion rate is much higher than the reaction rate; and b) when the diffusion rate is much lower than the reaction rate.

---

* Equation (7) in its outward form is identical with the empirical formula of A. I. Duntsess and A. V. Frost [2] for the kinetics of the self-inhibiting homogeneous monomolecular decomposition reactions of hydrocarbons. Equation (7) differs from Dintsess and Frost equation in that the constants β and M are derived rationally.

In the first case, the process kinetics will be wholly governed by chemical factors. Mathematically, this may be expressed as:

$$D \longrightarrow \infty: \quad \beta \longrightarrow 0$$

$$DSB\mu \gg kva; \quad M \longrightarrow k.$$

Thus, in the first case Equation (7) is transformed into the usual equation for the velocity of a first-order reaction.

In the second case, the reaction rate is mainly determined by the rate at which the reagent is supplied to the reaction zone, and the relationships are as follows:

$$DSB\mu \ll kva; \quad \beta \longrightarrow \frac{1}{a}; \quad M \longrightarrow \frac{DSB\mu}{va}.$$

Thus the limiting value of the coefficient of inhibition β equals $\frac{1}{a}$.

Strictly speaking, the coefficient of inhibition approaches $\frac{1}{a}$ but is not equal to it. If $\beta = \frac{1}{a}$, it would mean that $D = 0$, and hence the reaction would terminate at the surface layer of the grain.

Process kinetics are usually judged by the quantity of reacted solid substance, and not by the quantity of reacted reagent.

If m gram molecules of the reacting solid substance correspond to one gram molecule of reagent, and if the recovery (degree of conversion) x' is figured in parts of unity ($a = 1$), Equation (7) becomes:

$$\frac{1}{t} \ln \frac{1}{1 - x'} - \beta' \frac{x'}{t} = M. \qquad (10)$$

Here

$$\beta' = \frac{mvk}{DSB\mu + kv} = m\beta. \qquad (11)$$

In the limit, β' will approach m, and β will approach unity.

The equation of the reaction kinetics in a current of liquid or gas at constant pressure ought not to differ, in principle, from Equation (10), for, as G.M.Panchenkov [3] has pointed out, the reaction rate at constant volume is directly proportional to the rate in a current of liquid.

Equation (7) not only makes it possible to determine the degree of completeness of the reaction at any instant from two experimental points for different time values, but it also enables one to compute the values of the constant of first-order velocity and of the coefficient of diffusion from Equations (8) and (9). If experimental data are available for various temperatures, the possibility arises of computing the activation energies of the chemical reaction and diffusion. Unfortunately, however, the available experimental material is insufficient for such calculations.

CHECKING THE FORMULA AGAINST EXPERIMENTAL DATA

To check the formula we made use of the circumstance that the equation is

a straight line when plotted in $\frac{1}{t} \ln \frac{1}{1-x'} - \frac{x'}{t}$ co-ordinates. Hence, if the experimental data lie along a straight line when plotted in these co-ordinates, this testifies to the applicability of the equation. To cite all the examples that confirm Equation (10) would take too much space here, and we shall therefore confine ourselves to a few characteristic cases.

Roasting. Roasting consists of heterogeneous reactions between a solid or several solids and the gas phase.

During the roasting process the gaseous substances diffuse through a stratum of solid reaction products or a mixture of solid reaction products and inert materials.

In dissociating roasting, the diffusion of the gases through the crust takes place in one direction only.

Naturally, the gases encounter a certain resistance in the process of diffusion. But, since a highly porous material is usually formed during dissociation, and what is more, the grains are broken down into more or less small pieces during roasting, there is reason to believe that the growing crust will not affect the course of the reaction, and that the latter will proceed in accordance with a first-order equation.

Table 1

Kinetics of the Dissociative Roasting of Alunite

Roasting time, hours	3	4	5	6	7	8	10	12
Elimination of chemically combined water, %	38.5	50.0	57.7	65.3	73.1	77.0	84.5	88.4
k.....	0.162	0.173	0.172	0.176	0.187	0.183	0.186	0.179

Let us cite data on the roasting of alunite, in which the latter loses its chemically combined water, by way of illustration [4] (Table 1).

The constancy of the constant of velocity of the first order reaction is satisfactory down to 90% of disintegration.

In all other types of roasting, we have to deal with both the diffusion of the reacting gas into the granule and with the diffusion of the gaseous reaction products outward.

Plenty of data is available on the kinetics of reducing roasting. By way of illustration, the data of D.P. Bogatsky [5] on the reduction of nickel-aluminum silicate by carbon monoxide are plotted in Fig. 1. As the temperature is raised, the coefficient β increases, which indicates that the diffusion and reaction rates are commensurable. The growth of β is due to the fact that the temperature variation of the coefficient of diffusion is less marked than that of the reaction-rate constant. Equation (10) also covers the other data in that paper satisfactorily.

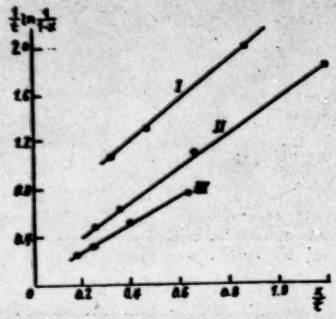

Fig. 1. Checking Equation (10) against data on the reducing roasting of nickel-aluminum silicate by carbon monoxide

I-Roasting temperature 800°, $\beta' = 1.7$; II-Roasting temperature 700°, $\beta' = 1.4$; III-Roasting temperature 600°, $\beta' = 1.2$.

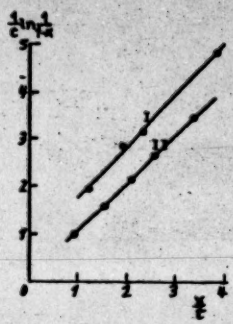

Fig. 2. Checking Equation (10) against data on the chlorination of wolfram ores by liquid sulfur chlorides.

Temperature 100°. I-artificial mixture, $\beta' = 1.1$; II-scheelite concentrate, $\beta' = 1$. Scale x 10

As an example of chlorination roasting covered by Equation (10), we may cite the data of Y.B.Fridman and Y. Bogarad [6] on the chlorination of wolfram ores by liquid sulfur monochloride (Fig. 2). In contradistinction to this, the chlorination roasting of polymetallic sulfide ore by gaseous chlorine at 300° apparently satisfies the equation for the velocity of a first-order reaction, according to the data of D.M. Chizhikov [7]. The computed values of the constants are as follows:

Time, min.	40	60	80	100	120
k_{PbCl_2}	0.020	0.024	0.022	0.020	–
k_{ZnCl_2}	–	0.014	0.013	0.011	0.012

Much data has been collected in our institute on oxidation, sulfating, and reduction roasting, all of which fully confirm Equation (10).

Leaching. The lixiviation reaction takes place between a solid and a liquid solvent. In the leaching process there is gradually formed a crust of inert lixiviated material, through which the fresh solvent diffuses into the reaction zone, the substance dissolved as the result of the reaction passing through in the opposite direction.

The leaching process resembles the process of dissolution of a solid body, and consequently many endeavors have been made [8,9] to apply Nernst's diffusion theory to it, as expressed by the following equation:

$$\frac{dx}{dt} = \frac{D}{\lambda}(\rho - \delta), \qquad (12)$$

where ρ = saturation concentration; and δ = volumetric concentration at time t.

Integration of this equation yields the usual equation for first-order kinetics. In actuality, the constant of leaching rate computed from a first-order equation does not remain constant, growing gradually but uninterruptedly smaller as time goes on. This is due to the fact that the analogy between dissolution and leaching processes is not far-reaching enough to enable the direct application of solution laws to the leaching process. As has been pointed out already, the main difference in principle consists of the gradual increase of the diffusion layer during leaching, whereas the thickness of the diffusion layer remains constant in the solution process.

It may be expected that Equation (10) is applicable to instances of leaching from fairly dense material. If the granule is porous enough, leaching, like roasting, can take place without inhibition in accordance with the first-order law. This assumption is graphically illustrated in Fig. 3, in which the leaching rate of two kinds of natural covellite and "artificial" covellite, obtained by the preliminary leaching of secondary mineral chalcocite,[10], is shown. "Artificial" covellite is much more porous than the natural mineral; it is leached out in a few days in accordance with the first-order equation, whereas the dense natural minerals are leached out in accordance with Equation (10), their leaching rate being limited by the diffusion. Kennecott covellite evidently has a higher coefficient of diffusion than that from Butte.

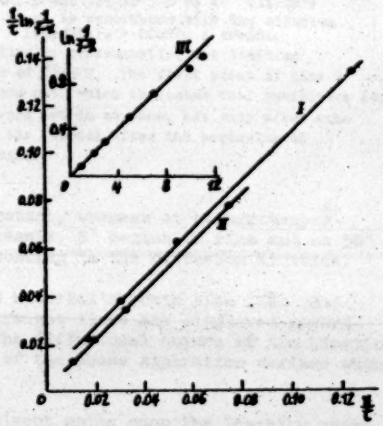

Fig. 3. Checking Equation (10) against data on the leaching rate of covellite in an acidulated solution of iron sulfate.

I-Kennecott covellite; II-Butte covellite; III-artifical covellite. Temperature 35° n = 1, β=1

One of the basic problems of lixiviation practice is the effect of temperature upon the leaching rate.

It is evident from Fig. 4, for the kinetics of the leaching of covellite, that the 50° straight line is shifted upward parallel to the 35° straight line [10].

Consequently, the kinetics of the lixiviation of CuS lie in the diffusion region under the conditions, and a rise in temperature results solely in an increase in the coefficient of diffusion.

The picture is somewhat different in Fig. 5 [10]. As the

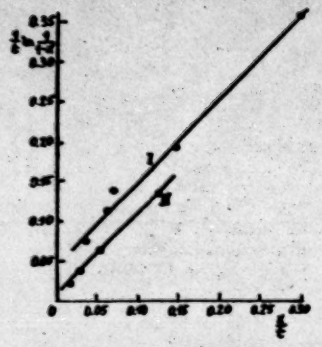

Fig. 4. Checking Equation (10) against data on the leaching rate of Kennecott covellite, −100+200 screen mesh, in an acidulated solution of iron sulphate.

I-50°; II-35°; n = 1, β' = 1

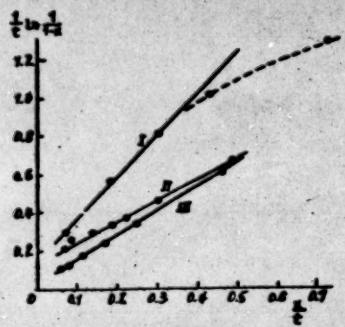

Fig. 5. Checking Equation (10). Effect of temperature on the leaching rate of chalcocite, −100+200 screen mesh, in an acidulated solution of iron sulphate.

I- 50°, β'=2; II-35°, β'=1.1; III-22°, β'=1.3. n, in accordance with the reaction $Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4$, equaling 2; consequently, the limiting value of $\beta' \to 2$. The first point of Line I dropped out, which indicates that inhibition does does not set in at once, but only after some time has elapsed after the beginning of leaching.

temperature rises, β' first drops and then rises again. This is evidently due to the fact that in this case, the variation of the coefficient of diffusion with temperature is greater at low temperatures than that of the velocity constant, whereas at higher temperatures the conditions are reversed; as a result, β' begins to rise and at 50° almost attains the limiting value, corresponding to the diffusion kinetics.

Fig. 6 illustrates the effect of the material's grain size [10]. As the degree of dispersion increases, the straight lines are displaced upward parallel to one another, which indicates the diffusional nature of the kinetics. The increase of M is linked to the growth of the phase separation surface with pulverization.

Fig. 7 shows the influence of the solvent anion upon the leaching rate [10]. Processing the experimental material in accordance with Equation (10) enabled us to prove that with iron sulfate, increased lixiviation is due not to the high rate of solution of the mineral in $Fe_2(SO_4)_3$ as compared with $FeCl_3$, but to the high coefficient of diffusion of $Fe_2(SO_4)_3$, which results in accelerating the lixiviation.

Equation (10) was likewise checked against other data, being completely substantiated.

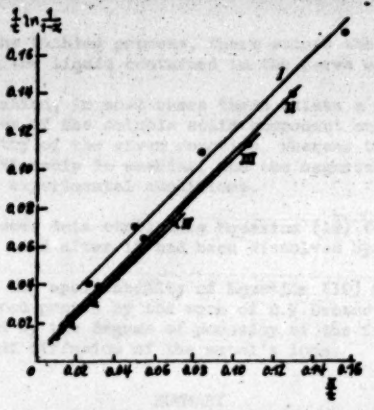

Fig. 6. Checking Equation (10). Effect of grain size upon the leaching rate of Kennecott covellite in an acidulated solution of iron sulfate.

I- 200 mesh; II-1pp + 200 mesh; III-18 + 28 mesh; IV-3 + 10 mesh; $\beta'=1$.

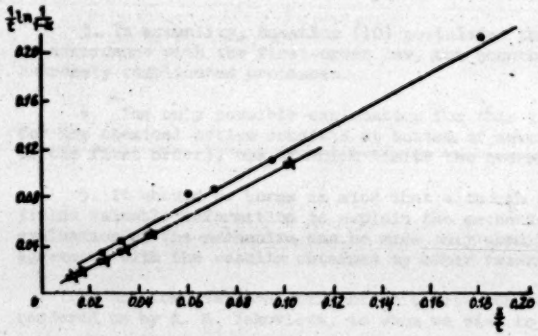

Fig. 7. Checking Equation (10). Influence of solvent upon the leaching rate of covellite, 200 mesh grain size.

I-1% solution of Fe as $Fe_2(SO_4)_3$ + 0.5% H_2SO_4; II-1% solution of Fe as $FeCl_3$ + 0.5%HCl; II-0-1% solution of Fe as FeCl; $\beta' = 1$; $n = 1$.

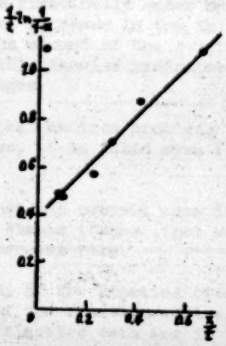

Fig. 8. Checking Equation 10 against data on the washing rate of leached sand containing gold as $KAu(CN)_2$. Intermittent washing. In the original the washing quantity is cited instead of the leaching time. $\beta' = 1.1$.

Washing. In the washing process, there occurs the diffusion of the substance dissolved in the liquid contained in the pores of the granule.

During lixiviation, in most cases there exists a well-known relationship between the molecules of the soluble solid component and the solvent, based upon the stoichiometry of the given reaction, whereas there is no fixed stoichiometric relationship in washing, and the magnitude of β' in Equation (10) depends on the experimental conditions.

Fig. 8 reproduces data confirming Equation (10) for the process of washing gold out of sand after it had been dissolved by potassium cyanide,[3].

Cementation. The applicability of Equation (10) to cementation processes may also be considered proved by the work of B.V.Drozdov. Inhibition of the reaction is governed by the degree of porosity of the film of cement metal and by the coefficient of diffusion of the metal's ions.

SUMMARY

1. All the examples cited, as well as a large number of computations made by us, indicate the applicability of the formula developed to processes of roasting, leaching, washing and cementation.

2. Despite all the differences between these various processes from the standpoint of chemical reactions, they may be collated kinetically under one generalized law based upon a calculation of the gradual increase in the thickness of the diffusing layer that is proportional to the amount of the reacted diffusing substance. The applicability of Equation (10) likewise indicates that most of these reactions take place in several stages.

3. In actuality, Equation (10) postulates that the reaction proceeds in accordance with the first-order law, but nonetheless, it is valid even for extremely complicated processes.

4. The only possible explanation for this is that the overall equation for the chemical action consists at bottom of several simple stages (that are of the first order), one of which limits the overall process rate.

5. It should be borne in mind that although study of the kinetics often yields valuable information to explain the mechanism of the reactions, final evaluation of the mechanism can be made only when the kinetics data are in agreement with the results obtained by other research methods.

In the computational part of this research considerable assistance was rendered us by A. M. Yakovleva, to whom we wish to express our gratitude.

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THE MOLECULAR STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF ORGANIC COMPOUNDS

I. THE BOILING POINTS OF THE HALOGEN DERIVATIVES OF THE AROMATIC SERIES

N. Kozlov

Molotov State Pedagogical Institute

The boiling point is a rigidly fixed physicochemical constant of many organic substances, as it is a property that characterizes the individuality of an organic compound. A vast amount of available experimental data on the boiling points of organic substances indicates clearly enough that this constant depends upon the molecular weight, the chemical composition, and structural factors of the molecule. Despite the large amount of research, however, it has not yet been possible to establish the variation of the boiling point with the foregoing factors quantitatively. Knowledge of the laws governing changes in the boiling point is of tremendous scientific and practical importance, since it would make it possible to penetrate more deeply into the molecular structure of organic substances and would assist in solving a number of practical questions facing our fuel industry.

Modern literature contains a large number of reports dealing with the investigation of boiling points. Among them is the research of Kopp [1], who advanced the hypothesis that this constant is an additive quantity and is determined by the molecular weight of the substance. The relationship between the boiling point and the critical temperature was established by the well-known Guldberg [1] rule, and its link with the heat of evaporation by the Truton formula [1]. The link of the boiling point with molecular surface was established by the research of Mokrushin [2], and with molecular refraction by the research of B. Nekrasov [3]. A number of empirical formulas have been proposed in recent research papers for calculating the boiling points of organic substances, principally the hydrocarbons, the most noteworthy of them being the papers by Nikolsky [4], Francis [5], Atenne [6], Barnot [7], Kinney [8], Merkel [9], Egloff [10], Kladsch [11], and Ufimtsev [12].

The author of the present paper made a critical survey of the work done on boiling points and came to the following conclusions.

1. Up to the present time the fundamental laws governing the variation of the boiling points of organic compounds with their molecular structure have not been discovered.

2. The empirical formulas proposed by various authors for calculating the boiling points of organic substances contain artificially derived

coefficients, which yield only approximate results in computation and are useless for reaching any conclusions regarding the structural peculiarities of the molecule.

3. It follows from what has just been said that there is no proper criterion in contemporary chemical literature to govern the selection of experimental data, and as a result our handbooks are full of extremely contradictory experimental data on the boiling points of organic substances.

All this led us to undertake the present research, the goal of which is the disclosure of the fundamental laws governing changes in the boiling point particularly in compounds of the aromatic series. We have employed a method developed by us, which is based upon the three following principles.

First Principle. The molecule of an aromatic compound is viewed as consisting of a given number of structural elements, which interact physicochemically with one another in complicated ways. Their number, chemical nature, and the nature of their chemical interactions determine the physicochemical properties of the substance. Numerous aromatic compounds may be looked upon as substitution products, with the hydrogen atoms of the benzene ring replaced by various other atoms or radicals. We may consider any aromatic substance to be a compound consisting of various structural elements, among which are the benzene ring and the atoms or groups attached to it. For example, toluene is a compound consisting of two elements: the remnant of the benzene ring , the phenyl radical C_6H_5, and the methyl group CH_3. Toluidine is a compound consisting of three structural elements, viz,: the remnant of the benzene ring C_6H_4, the methyl group CH_3, and the amino group NH_2. But how can we determine the influence of each structural element upon the boiling point?

In view of the fact that the b.p. of benzene is 80.05°, whereas the b.p. of cyclohexane, which can be synthesized by adding six hydrogen atoms to benzene, is 80.80°, we conclude that changing the number of hydrogen atoms in the ring does not involve any appreciable change in boiling points; we therefore assume that the effect of the ring hydrogen atoms upon the boiling points of benzene and cyclohexane is extremely insignificant. We shall therefore ascribe every increase in the boiling point observed for any monosubstituted derivative of benzene over that of benzene itself entirely to the presence of the second element in the molecule.

Thus, taking the boiling point of benzene itself as that of the benzene ring element, we are able concretely to establish the effect upon the boiling point of any substituent attached to the benzene ring. The concrete value of the coefficient expressing the effect of each benzene-ring substituent is determined as the difference between the experimentally measured boiling point of the corresponding monosubstituted derivative and that of benzene:

$$K = A - B, \qquad (1)$$

where K is the coefficient for any substituent in the benzene ring, A is the boiling point of any monosubstituted derivative of benzene, and B is the boiling point of benzene, the coefficient of the benzene ring.

Using Equation (1), we shall now compute the coefficients of the boiling-point effect of all sorts of substituents attached to the benzene ring; they show that when the hydrogen of the benzene ring is replaced by any substituent whatsoever, the rise of the boiling point above that of benzene equals the

coefficient for the given substituent. Coefficients computed by us for various benzene-ring substituents are listed in Table 1.

TABLE 1

Benzene ring	CH_3	C_2H_5	n-C_3H_7	iso-C_3H_7	Cl	Br	I	OH	NO_2
80.05	30.60	56.10	79.20	74.40	51	76	108	102	131

Second Principle. The boiling point of aromatic compounds is an additive property, determined by the properties of the individual structural elements that go to make up the given molecule.

This principle is likewise derived from experimental data on the boiling points of organic compounds. In accordance with this principle, the boiling point is the sum total of the coefficients of all the structural elements that go to make up the given molecule:

$$T = An + B_n + C_n + D_n, \qquad (2)$$

where n is the number of structural elements involved.

Unfortunately, in actuality, the number of aromatic compounds for which the experimentally determined boiling point fully coincides with that calculated from the additivity rule is extremely small.

Third principle: In a very large number of instances, the boiling point measured experimentally differs quite markedly from that computed from the additivity rule expressed in Equation (2). For example, hexaethylbenzene's boiling point is 298° according to the experimental data, whereas its boiling point computed from the additivity rule of Equation (2) would be:

$$T = 80.05 + (56.10 \times 6) = 416.65°.$$

We consider the reason for so wide a discrepancy between the experimentally measured boiling point and that computed theoretically to be the influence upon the boiling point of the interactions among the substituents attached to the ring. And in fact, in any monosubstituted derivative of benzene the only interaction present is that between the ring and the substituent, the influence of their interaction being allowed for in the coefficient derived for this substituent. An altogether different situation obtains when we introduce a second substituent into the benzene ring; then we also have to deal with the interaction between the substituents. The latter may affect each other quite pronouncedly; in many instances this may result in a structural change of the substituents, as is observed, for example, in the formation of hydrogen bonds. The mutual influence of the substituents upon each other is reflected in the physicochemical properties of the substance, including its boiling point; that is why, whenever we observe a departure of the experimentally observed boiling point from that computed from the additivity rule, we ascribe the discrepancy to the effect of the interaction of the substituents upon the boiling point. If these notions be taken as a basis, the coefficient of the effect of substituent interactions upon the boiling point is the difference between the two following quantities: the boiling point determined by the

additivity rule of Equation (2) and that found experimentally for the compound:

$$a = T_{addit.} - T_{experim.}$$

In the investigation of the boiling points of ortho, meta, and para isomers, the discrepancy between the experimental values and those computed from the additivity rule represents the influence of the interaction between pairs of substituents located at various positions on the benzene ring. In polysubstituted benzene derivatives, this discrepancy is the sum of the effects upon the boiling point of the interactions of all the substituents with one another.

We have established an extremely important fact indicating the regular nature of the effect of substituent interactions upon the boiling point. It has been established that, if to a pair of substituents in the benzene ring there is added a third, a fourth substituent, and so forth, the effect of the interaction between each pair of substituents remains unchanged (except for specially limited cases), the sum total of possible interactions between pairs of substituents increasing proportionally to the total number of substituents.

Hence, starting with the experimental data for the boiling points of disubstituted benzene derivatives, we can calculate quite accurately the extent of the effect upon the boiling point of the interaction between two substituents as a function of their position in the ring.

The values of the coefficients of the effect of interaction between substituent pairs upon the computed boiling point, as computed by us, proved to be as follows (Table 2):

TABLE 2

Position of the substituent	CH_3–CH_3	CH_3–C_2H_5	CH_3–Cl	CH_3–Br	CH_3–I	CH_3–F
ortho-	+3.25	-2.0	-3.0	-6.6	-8.6	-2.6
meta-	-2.05	-5.25	-1.0	-3.6	-5.6	0
para-	-2.85	-4.25	-1.0	-3.0	-5.0	0

Position of the substituent	Cl–Cl	Br–Br	Cl–I	F–F	Cl–Br	Br–I
ortho-	-2.0	-7.0	-7.0	-1.5	-4.0	-8.0
meta-	-8.0	-11	-12	-6.0	-10	-13
para-	-8.0	-12	-14	-2.0	-11	-13

We can now set down the final formula for computing the boiling points of aromatic compounds, which will look like this:

$$T = A_n + B_n + Cn \ldots \pm (a_n + b_n + c_n). \qquad (3)$$

where A, B, and C... are the coefficients for the structural elements of the molecule; a, b, c,... are the coefficients for the influence of substituent interactions upon the boiling point; and n is the number of structural elements

or the number of identical combinations of substituents.

To illustrate the practical application of this method of ours, let us consider the calculation of the boiling point of 2-chloro-3-nitrotoluene.

According to the literature data [13], the boiling point of 2-chloro-3--nitrotoluene is 263°. Computed by the additivity rule, as set down in Equation (2), its boiling point would be:

$$T = 80.05 + 30.60 + 131 + 51 = 292.65°,$$

where 80.05 is the coefficient for the benzene ring, 30.60 is the coefficient for the CH_3 group, 51.0 is the coefficient for the chlorine atom, and 131 is the coefficient for the NO_2 group. Consequently, the discrepancy between the experimentally measured boiling point and that computed is:

$$292.65 - 263 = 29.65°.$$

From what has already been said it follows that the value of 29.65° is the total effect of the interactions of all the benzene-ring substituents. It is evident from the structural formula for the compound under consideration that the substituents react on one another in the following forms: CH_3 and Cl in the ortho position; CH_3 and NO_2 in the meta position; and Cl and NO_2 in the ortho position. All these three substituent interactions will affect the boiling point computed from the additivity rule. But how are we to determine the effect of each substituent pair upon the boiling point? We do this by means of the following method. We know from the literature [13] that the b.p. of o-chlorotoluene is 158.6°. B.p. computed is 161.6°. Hence, the discrepancy between the computed and the experimentally determined boiling points is:

$$161.6 - 158.6 = 3°.$$

This is the coefficient of the effect of the interaction between the substituents CH_3 and Cl when in the ortho position. This value remains without any noticeable change in any compound where the CH_3 and Cl groups are in the ortho position, no matter whether other substituents are also present or not.

Further, the boiling point of m-nitrotoluene is 231° according to the literature. The b.p. computed from the additivity rule is 241°. Consequently, the discrepancy between the computed and experimentally determined boiling points is 10°. It follows that the interaction between the CH_3 and NO_2 groups in the meta position lowers the boiling point computed from the additivity rule by 10°, which thus is the coefficient of the effect of the interaction between these groups whenever they are in the meta position with respect to each other in the benzene ring.

According to the literature data, o-chloronitrobenzene has a b.p. of 246°, whereas the b.p. computed from the additivity rule is 262°. The discrepancy is 16°. We assign this value as the effect of the interaction of the Cl and NO_2 groups in the ortho position with respect to each other. We believe that no matter what compound these groups are in, they will lower the boiling point by 16° if they are in the ortho position. Thus we establish the degree of influence of substituent interaction upon the boiling point.

We can now apply the required corrections to the boiling point of 2-chloro-3-nitrotoluene, computed from the additivity rule. Allowing for the

effect of substituent interactions, we can compute the actual boiling point, which will then be:

$$T = 80.05° + 30.6 + 51 + 131 - (3 + 10.6 + 16) = 263.05°,$$

which practically coincides with the value found experimentally.

Thus the coefficients of the effect of the interaction of any substituents upon the boiling point can be determined. We think it necessary to emphasize again that, despite the fact that the coefficients of the effect of substituent interaction upon the boiling point are derived from the experimental data for a disubstituted derivative of benzene, they retain their value for polysubstituted benzene derivatives. This type of recurrence of the value of these coefficients in the polysubstituted derivatives of benzene, which are of a rigidly regular nature, indicates the universal value of these coefficients and the possibility of their extensive application. This repeatability likewise indicates the periodic nature of this relation. Because of this we must acknowledge that the coefficients proposed by us reflect the actual relationships of the structural elements within the molecule; this is why we consider them also applicable in reaching conclusions concerning the structural peculiarities of the molecules of organic substances.

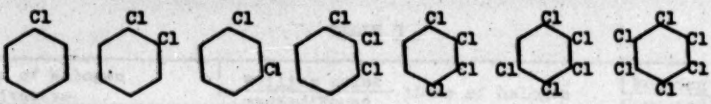
Using the coefficients derived by us and Equation (3), we computed the boiling points of a great variety of aromatic compounds and confirmed the fact that the formula proposed by us is fully applicable in computing the boiling points of aromatic compounds with experimental accuracy. The method suggested by us makes it possible to disclose the fundamental laws governing the change in the boiling point of all sorts of aromatic compounds as a function of the molecular weight, the chemical nature of the substituents, the molecular structure, and the interactions between the substituents within the molecule. The material now available to us convinces us that the method we have suggested makes it possible to discover the fundamental laws governing the variation of other physicochemical constants of organic compounds, such as: specific gravities, heats of combustion, refractive indexes, etc.

The coefficients of the effect of substitutent interaction found by us reflect the presence in the molecule of the intramolecular process of substituent interaction, which affects the physicochemical properties of the substance in general and the boiling point in particular. The coefficients proposed by us are a unique standard of measurement of this effect, and their study therefore makes possible a deeper understanding of the nature of some intramolecular processes that take place within the molecules of organic substances.

The method proposed by us is based upon the assumption of intramolecular interaction between substituents, which is nothing new in organic chemistry. It will suffice to mention the well-known research of V.V.Markovnikov [14] on the reciprocal influence of the atoms in the molecule of an organic substance. Among recent papers, the interesting research of Tishchenko [15] is worthy of note. After the discovery of hydrogen bonds, there can no longer be any doubt whatever concerning the interaction between substituents within the molecule. Study of the boiling points of organic compounds enables us to find a unique quantitative method of measuring this interaction.

The boiling points of halogen derivatives of benzene and toluene have

been investigated in the present paper. When the halogen derivatives are arranged in a series in order of increasing molecular weight, a certain regularity is noticed in the change of their boiling points; this is graphically shown in the following examples:



Experimental b.p. ..	131°	179°	173°	219	254°	277°	309°
Rise in b.p. per atom of chlorine	51°	49°	46°	43°	43°	39°	38°

This regularity consists in the fact that an increase in the number of halogen atoms in the molecule causes the boiling point to rise uninterruptedly, but not always by the same amount. Because of the latter circumstance it is difficult to express the law governing variation of the boiling points of compounds of this series in a precise mathematical form. The basic reason for the irregular variation of the boiling points of halogen derivatives is the fact that both the structural factors and the factors of the mutual influence of the substituents act upon the boiling point; this is why we resolved to employ our method to establish the relationship between physicochemical properties and molecular structure.

As in our previous paper on the boiling points of the aromatic hydrocarbons [17], we consider that the boiling point of halogen derivatives is also an added property, which is affected by the nature of the substituents and their interactions. First let us use the method described above to find the coefficients of both the main structural elements of the molecules of halogen derivatives of benzene, and the coefficients of the effect of the interaction of the halogen atoms with one another and with the methyl group upon the boiling point. The values of the coefficients found by us are listed in Tables 1 and 2. With these derived coefficients and Formula (3), we calculated the boiling points of the halogen derivatives. In our calculation of the boiling point of a given halogen derivative all the theoretically possible substituent interactions within this substance were considered, as may be graphically shown by the following example. Commercial tetrachlorobenzene has a boiling point of 254° according to the literature data [13]. There are five structural elements in its molecule: the skeleton of the benzene ring and four chlorine atoms. The following relationships are possible among the substituents: three ortho positions, two meta positions, and one para position. The computed boiling point would then be:

$$T = 80.05 + (51 \times 4) - [(2 \times 3) + (8 \times 2) + (8 \times 1)] = 254.05°.$$

The results of our calculation of the boiling points of the halo derivatives are listed in Table 3. These data again confirm the complete serviceability of our formula in computing the boiling points of halo derivatives. In

the overwhelming majority of cases the discrepancy between the experimental and the computed data lies within the limits of experimental error. The reason for the very large discrepancy in the case of hexachlorobenzene is still unclear..

TABLE 3

Name of halogen Derivative	Boiling point Computed	Found
Chlorine Derivatives		
1,2,3-Trichlorobenzene	221°	218-219°
1,2,4-Trichlorobenzene	215°	213
1,3,5-Trichlorobenzene	209	208.5
1,2,3,4-Tetrachlorobenzene	254	254
1,2,4,5-Tetrachlorobenzene	248	243-246
1,2,3,5-Tetrachlorobenzene	248	246
Pentachlorobenzene	279	276
Hexachlorobenzene	302	309
2,3-Dichlorotoluene	206	194-195
		204-206
2,4-Dichlorotoluene	200.6	198
		200
2,5-Dichlorotoluene	200.6	200
3,4-Dichlorotoluene	208.6	205-207
3,5-Dichlorotoluene	202.6	201-202
2,6-Dichlorotoluene	198	198
2,4,5-Trichlorotoluene	240.6	231
3,4,5-Trichlorotoluene	248.6	247
2,3,5,6-Tetrachlorotoluene	270	271-276
Pentachlorotoluene	300.6	301
4-Chloro-o-xylene	193.5	191.5
3-Chloro-o-xylene	191.5	189.5
2-Chloro-m-xylene	183.15	185-187
4-Chloro-m-xylene	185.2	187-188
5-Chloro-m-xylene	188.2	190
2-Chloro-n-xylene	185.4	183-188
1,2,Dimethyl-3,5-dichlorobenzene	232.5	226
1,3,Dimethyl-2,4-dichlorobenzene	223.2	223
1,3-Dimethyl-2,6-dichlorobenzene	225.2	223
1,4-Dimethyl-2,5-dichlorobenzene	224.4	222
1,2,Dimethyl-3,6-dichlorobenzene	230.5	227
1,2-Dimethyl-3,4-dichlorobenzene	240.5	{227 {240
1,2-Dimethyl-3,5-dichlorobenzene	238.5	234

Name of halogen derivative	Boiling point Computed	Found
1,2,4-Trimethyl-3-chlorobenzene	214.2°	213°
1,3,5-Trimethyl-2-chlorobenzene	209.7	206
1,2-Dimethyl-3,5,6-trichlorobenzene.	269.5	230-240
1,2-Dimethyl-3,4,5-trichlorobenzene.	272.5	265
1,3-Dimethyl-2,4,5-trichlorobenzene.	262.2	225-255
1,3-Dimethyl-2,4,6-trichlorobenzene.	254.2	233
1,3-Dimethyl-4,5,6-trichlorobenzene.	291.2	323
1,3,5-Trimethyl-2,4-dichlorobenzene..	245.6	244
1,3,5-Trimethyl-2,4,6-trichlorobenzene	273.6	280
1,2,3,4-Tetramethyl-5-chlorobenzene..	249	240
1,2,4,5-Tetramethyl-3-chlorobenzene..	242	237
1,2,3,4-Tetramethyl-5,6-dichlorobenzene	293.2	280
1,2,4,5-Tetramethyl-3,6-dichlorobenzene	277	275
Bromine Derivatives		
1,2,3-Tribromobenzene	283	-
1,2,4-Tribromobenzene	278	276
1,3,5-Tribromoseltzer	275	278
1,3,4,5-Tetrabromobenzene	325	329
Hexabromobenzene...	316	316
2,5-Dibromotoluene.	240.4	236
2,4-Dibromotoluene.	242	243
		275

TABLE 3 (Continued)

Name of halogen derivative	Boiling point Computed	Boiling point found
2,6-Dibromotoluene....	239.4°	244°
3,4-Dibromotoluene....	249	241
3-Bromo-o-xylene.....	210.2	206-213
4-Bromo-m-xylene.....	205.5	205
1,2-Dimethyl-3,4-dibromobenzene.....	273.6	277
1,2-Dimethyl-4,5-dibromobenzene.....	276.2	278
5-Bromo-m-xylene.....	208	206
1,3-Dimethyl-2,4-dibromobenzene.....	257.4	269
1,3-Dimethyl-4,5-dibromobenzene.....	267.4	257
1,3-Dimethyl-4,6-dibromobenzene.....	261	255
2-Bromo-p-xylene.....	204	205
1,4-Dimethyl-2,5-dibromobenzene.....	258	261
1,4-Dimethyl-2,3,4,5-tetrabromobenzene...	357.5	355
1,2,4-Trimethyl-3-bromobenzene.....	229	226-229
1,2,4-Trimethyl-5-bromobenzene.....	233	233
1,2,4-Trimethyl-6-bromobenzene.....	232.5	223-228
1,2,4-Trimethyl-3,6-dibromobenzene.....	280.5	293
1,3,5-Trimethyl-2-bromobenzene.....	226	225
1,3,5-Trimethyl-2,4-dibromobenzene.....	290	276-278 285
1,2,3,4-Tetramethyl-bromobenzene.....	268.7	265
1,2,3,5-Tetramethyl-4-bromobenzene.....	260	254
1,2,4,5-Tetramethyl-3-bromobenzene.....	258.7	262
1,2,4,5-Tetramethyl-3,6-dibromobenzene..	292	290
Iodine Derivatives		
2,4-Diiodotoluene.....	302	296
4-Iodo-o-xylene.....	241.9	230
4-Iodo-m-xylene.....	223.5	220-230
2-Iodo-m-xylene.....	230	230
5-Iodo-m-xylene.....	256	235
2-Iodo-p-xylene.....	232.7	217 230-235

Name of halogen derivative	Boiling point Computed	Boiling point Found
1,3,5-Trimethyl-2-iodobenzene.....	251.5	250
1,2,4,5-Tetramethyl--3-iodobenzene.....	279	285-289
2,3-Dichlorobromobenzene.....	242	243
2,4-Dichlorobromobenzene.....	235	235
2,5-Dichlorobromobenzene.....	236	235
2,6-Dichlorobromobenzene.....	242	242
3,5-Dichlorobromobenzene.....	230	232
2,3-Dibromochlorobenzene.....	269	264
3,4-Dibromochlorobenzene.....	255	256
2,6-Dibromochlorobenzene.....	264	265
2,4-Dibromochlorobenzene.....	257	258
3,5-Dibromochlorobenzene.....	252	256
2,5-Dibromochlorobenzene.....	257	259
2-Chloro-4,6-dibromotoluene.....	270	275
2,3,5-Trichloro-4-bromotoluene.....	295	265-275
1,2-Dimethyl-3,5-dichloro-4-bromobenzene.....	292.8	270
2,5-Dichloroiodobenzene.....	264	250 255-256
2,4-Dichloroiodobenzene.....	267	255-257 262-263
2,4,6-Trichloroiodobenzene.....	289	297
4-Bromo-2-iodotoluene	270	262-266
5-Bromo-2-iodotoluene	269	265
2-Bromo-4-iodotoluene	270	267
3-Bromo-4-iodotoluene	278	265
3,5-Dibromo-4-iodotoluene.....	331	270
3,5-Dibromo-2-iodotoluene.....3	322	314 (decomp)

TABLE 3 (contd.)

Name of halogen derivative	Boiling point	
	Computed	Found
4-Chloro-2-iodotoluene	249	243
4-Chloro-3-iodotoluene	258	249
5-Chloro-2-iodotoluene	247	240
2-Chloro-5-iodotoluene	246	240

The data of Table 3 yield quite interesting conclusions. We notice that when the methyl group interacts with chlorine or fluorine atoms the additive computation of the boiling point changes very slightly. And even if this slight influence of this interaction is noted, it is found to exist only when these groups are in the ortho position. The interaction of the methyl group with bromine or iodine is reflected quite noticeably in the boiling points computed by the additivity rule.

Comparing the data on the interaction of the methyl group with the halogens for the meta-substituted derivatives, we find that the nature of the effect upon the boiling point of the CH_3 and I groups is contrary to the effect exerted by the CH_3 and F, CH_3 and Cl, or CH_3 and Br groups. This is seen from a comparison of the coefficients of these groups in the meta position. That is why, starting with the closeness of the halogen's chemical properties in general, we are inclined to assume that even in the case of m-iodotoluene, the nature of the boiling-point effect must be the same as that of the other halogens, and, hence, that the boiling point cited in the literature for m-iodotoluene was determined incorrectly; it should actually be considerably higher, 212° instead of 204°. And in fact, recent research has shown that m-iodotoluene's boiling point is 213°; then the coefficient of the effect of the interaction of the CH_3 and I groups in the meta position will be -5.6°, which corresponds to the nature of the derived law governing the variation of boiling points in the halogen toluene series.

It may be concluded from the material we have studied that a halogen atom exerts the greatest influence upon the methyl group in the ortho position, this influence increasing with the halogen's atomic weight.

The interaction of the halogens with one another exerts a quite considerable influence upon the boiling point computed from the additivity rule. This influence is greatest when the halogen atoms are in the meta and para positions, and least when they are in the ortho position. The intensity of interaction between the halogens depends upon their atomic weights; the interaction increases with increasing halogen atomic weight.

Our confidence in the correctness of our formulas justifies our applying them in calculating the boiling points of halogen derivatives whose boiling points are still not established. We chose as our examples the halo derivatives of ethylbenzene, for which the boiling points of only a few compounds are known, as shown by the following data [13] (Table 4 - p. 321).

To do this, we use the boiling point of p-chloroethylbenzene to find the coefficient of the influence of the interaction of the C_2H_5 and Cl groups in the para position; the value found was 6°.

TABLE 4

Name of halogen derivative	Boiling point	
	Found	Computed
o-Chloroethylbenzene	–	178°
m-Chloroethylbenzene	–	181
p-Chloroethylbenzene	181°	181
2,5-Dichloroethylbenzene	214	215
2,3-Dichloroethylbenzene	–	221
3,5-Dichloroethylbenzene	–	218
Pentaethylchlorobenzene	286	290
2,3,4-Trichloroethylbenzene	–	256
2,3,4,6-Tetrachloroethylbenzene	270-275	274
Pentachloroethylbenzene	300	299
3,6-Dichloro-1,2,4-Triethylbenzene	270-276	271.8°
2,4,5,6-Tetrachloro-1,3-diethylbenzene	290	282.3
3,6-Dichloro-1,2,4,5-tetraethylbenzene	296	287.8

Furthermore, the boiling point of 2,5-dichloroethylbenzene is experimentally found to be 214°, whereas the boiling point is computed to be 238.1° from the additivity rule; the difference of 24° is determined by the interaction between the substitutents, namely, C_2H_5 and Cl, in the ortho and meta positions, and the two chlorine atoms in the para position.

The effect of the interaction of chlorine atoms in the para position upon the boiling point is 8°, as we know from what has already been set forth, whence the aggregate effects of the interaction of two chlorine atoms with the ethyl group equals 24 – 8 = 16°. Hence, we have to find out the effect upon the boiling point of the interaction of the chlorine atom with the ethyl group in the meta and ortho positions. By analogy with the nature of the boiling-point effect of the interaction between the chlorine atom and the methyl group, in accordance with which it is identical for the meta and para positions and somewhat higher for the ortho position, we assume that the coefficients of the effect of interaction for the C_2H_5 and Cl groups are nine degrees in the ortho position and six degrees in the meta position. Using the coefficients thus obtained, we computed the boiling points of various chloroethylbenzenes; our results are listed in Table 4. We have no doubt that the data we thus possess on the boiling points of the halo derivatives of ethylbenzene are in agreement with the real values.

Thus, in the example discussed above we were able to prove that it is possible to establish the value of the coefficients of the effect of substituent interaction upon the boiling point even with highly inadequate information on the boiling points of some classes of organic compounds, and to use them to calculate the boiling points of as yet unknown compounds. The method we suggest for studying the boiling points of organic compounds makes possible free orientation in the contradictory experimental material on the boiling points of halogen derivstives accumulated by contemporary organic chemistry.

In the light of the notions set forth above we cannot accept as correct the experimental data on the boiling points of the following compounds: 2,4,5-trichlorotoluene; 1,2-dimethyl-3,4,5-trichlorobenzene; 1,3-dimethyl-2,4,6-trichlorobenzene; 4-iodo-o-xylene; 2,3,5-trichloro-4-bromotoluene; 1,3-dimethyl-2,4,5,6-tetrachlorobenzene; as well as a number of other compounds, as is evident

from the data of Table 3.

Among the various contradictory experimental figures given by different authors for the same compound our method makes it possible to establish the best value: thus, the boiling point of 1,2-dimethyl-3,4-dichlorobenzene is given by different authors as 222° and 240°; our calculation indicates that the latter value is correct.

The boiling point of 1,3-dimethyl-2,4,5-trichlorobenzene has been measured as 225° and 255°; our calculation indicates that the second value is correct. The boiling point of 2,4-dibromotoluene is reported as 243° and 275°; as we see it, the first value is correct.

SUMMARY

1. The method suggested by us has made it possible to establish the basic laws governing the variation of boiling points in a number of halogen derivatives of the aromatic series. The boiling point of such compounds is an additive property, which is affected by the interaction of the substituents attached to the benzene ring. The degree of this influence depends on the chemical nature of the substituents, their number, and their position in the molecule. We have been able to establish quantitatively the boiling-point effect of the interaction of hydrocarbon radicals with the halogens and of the halogens with each other, as computed by the additivity rule.

2. A formula and coefficients are proposed for calculating the boiling points of halogen aromatic derivatives, their serviceability being confirmed by a large amount of factual material.

3. It has been proved in special investigations that the proposed method is fully serviceable for the exact computation of the boiling points of as yet unknown halogen derivatives of the aromatic series.

4. This proposed method makes possible free orientation in the vast amount of experimental material on the boiling points of organic compounds that has been accumulated by contemporary organic chemistry, and to establish the value that is most correct among contradictory experimental data.

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THE PHYSICOCHEMICAL PROPERTIES OF ORGANIC COMPOUNDS AS A FUNCTION OF MOLECULAR STRUCTURE

II. STRUCTURE AND REFRACTIVE INDEX OF HYDROCARBONS OF THE METHANE SERIES

N. Kozlov

Molotov State Pedagogical Institute

As we know, the question of the variation of the physico-chemical properties of organic compounds with the structure of their molecules is one of the most important problems of contemporary physical and organic chemistry. A large number of special investigations have been devoted to this problem, finding expression in a series of monographs, [1,2].

In previously published papers the present author succeeded in developing a method that establishes a relationship between the boiling points of organic compounds and the structure of their molecules. At that time the author expressed the conviction that the method he proposed is entirely serviceable for studying the relationship between the molecular structure of organic substances and their other physicochemical properties, namely: specific gravity, heat of combustion, parachor, etc.

The present paper is an endeavor by the author to develop a quantitative theory of the variation of the refractive index of the hydrocarbons of the methane series with the structure of the chain of carbon atoms and the interactions of the molecule's structural groups with one another.

We believe that this kind of investigation may possess scientific and practical interest. The theoretical significance of research on the refractive index is that the latter is used in studying the phenomena of dispersion and polarization of molecules [2]. The practical significance of this type of research may be seen from the fact that in recent years refractometric methods of analysis of petroleum products have been vigorously developed, and have proved to be extremely valuable in the analysis of the chemical composition of gasolines [4,5]. In view of the fact that we have not yet been able to establish a relationship between the refractive index and structure [6], we considered it desirable to do research in this field.

In our study of the refractive index of methane hydrocarbons we were guided by the following considerations: in molecules of organic compounds the individual chemical atoms are linked together in a definite manner in composite structural groups; the latter include hydrocarbon radicals and functional

groups. As a result of the given link between the atoms in a structural group, the latter possesses specific properties; for example, the carboxyl group determines acidity, the amino group basicity, etc. The structural groups within the molecule interact with one another in a complex fashion; this also affects the substance's physicochemical properties. It follows that the physicochemical properties of organic substances will be determined by the chemical composition of the molecule, and by the number, chemical nature, and interactions of the structural groups comprising the given molecule.

In some cases, it has been possible to express some properties of individual atoms and structural groups experimentally as definite quantities, the given property of the molecule as a whole being expressed as the sum total of the corresponding quantities that are characteristic of the individual atoms and structural groups. This is the state of affairs in the determination of molecular refraction, parachor, heat of combustion, etc.

With these considerations as our guide in the investigation of the refractive index, we endeavored to determine the aggregate number of structural groups in the molecule, their interactions within the molecule, and their effect upon the substance's physicochemical properties.

All the methane hydrocarbons, which have a normal carbon chain, are the simplest compounds structurally, compared to their isomers, but as a methane hydrocarbon of normal structure may be transformed into any isomer, we took the experimental data on the refractive indexes of normal hydrocarbons as a basis for all subsequent measurements. These values are listed in Table 1.

Table 1

Hydrocarbon	n_D^{20}	Homologous Difference
n-pentane	1.3576	-
n-hexane	1.3750	0.0174
n-heptane	1.3877	0.0127
n-octane	1.3976	0.0099
n-nonane	1.4056	0.0080
n-decane	1.4114	0.0062

Then, by comparing the refractive indexes of normal hydrocarbons with the refractive indexes of their isomers, we are able to ascertain with perfect clarity that to any given type of change in the structure of the carbon chain there corresponds a rigidly determined change in the refractive index as against the value of that index for a compound of normal structure. Hence, every structural change in the chain produces a rigidly determined effect upon the refractive index, which may be measured by the difference found by computing the refractive index of the isomer from the refractive index of the compound with a normal carbon-atom chain.

We found that these differences are extremely regular, and we have adopted them as coefficients of the effect of given structural factors of the molecule upon the refractive index.

We obtained the following values for the effect of structural factors upon the refractive index: (see following page).

In addition, the intramolecular interaction of the groups with one another also affects the refractive index of an organic substance. We found that when

Structural type	Effect upon refraction compared to hydrocarbon of normal structure
I.	Decrease of 0.0025
II.	Increase of 0.0011
III.	Increase of 0.004, etc., without change
IV.	Increase of 0.0040, etc., without change.
V.	Decrease of 0.0050
VI.	Increase of 0.0022
VII.	Increase of 0.0030.

there are methyl groups in the molecule, which may be looked upon as substituents attached to the carbon chain, an effect of their interaction with each other upon the refractive index is observable only when they are attached to adjacent carbon atoms, i.e., in the position they raise the refractive index by 0.0050.
When the methyl groups are
in the 1,3 or 1,4 positions, etc., their interaction exerts no observable effect upon the refractive index.

The coefficients of the effect of structural factors and of substituent-interaction factors upon refraction derived by us reflect the functional relationships existing between molecular structure and refractive index.

On the basis of what has been set forth above we worked out a formula for computing the refractive indexes of saturated iso-hydrocarbons, as follows:

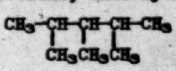
$$R = R' \pm (an + bn + cn.....), \qquad (1)$$

where R' is the refractive index of the normal hydrocarbon; R is the refractive index of the isomer; a, b, c.... are the coefficients of the effect of structural factors and group interactions upon refraction; and n is the number

of identical structural factors of forms of substituent interaction.

Formula (1) may be used to calculate the refractive indexes of the hydrocarbons of the methane series no matter what their structure. This can be vividly demonstrated by calculating the refractive index of 2,3,4-trimethylpentane, which is $n_D^{20} = 1.4043$ according to experimental data.

According to our notions, this hydrocarbon



has two structures of Type (I) and one structure of Type (II); moreover, owing to the interaction of the methyl groups in the 2,3,4 positions with each other, there are two identical types of interaction of the groups. Thus, using the coefficients we have derived for these factors, we find the theoretical value of the refractive index to be:

$$n_D^{20} = 1.3976 \pm (-0.0025 \times 2) + (+0.0011 \times 1) + (+0.0050 \times 2) = 1.4037.$$

We have computed the refractive indexes of several methane iso-hydrocarbons by this method, the results being tabulated in Table 2. The experimental data on the refraction of methane hydrocarbons cited in Table 2 were taken from the hydrocarbon handbook edited by Doss, [7].

Table 2

Refractive Indexes of Iso-Hydrocarbons of the Methane Series

Hydrocarbon	Experimental	Calculated	Hydrocarbon	Experimental	Calculated
2-Methylpentane	1.3715	1.3725	3-Methylnonane	1.4125	1.4125
3-Methylpentane	1.3766	1.3761	4-Methylnonane	1.4123	1.4128
2,3-Dimethylbutane	1.3750	1.3750	2,4-Dimethyloctane	1.4090	1.4093
2-Methylhexane	1.3849	1.3852	2,6-Dimethyloctane	1.4107	1.4100
3-Methylhexane	1.3887	1.3888	2,2-Dimethyloctane	–	1.4064
2,2-Dimethylpentane	1.3921	1.3921	2,3-Dimethyloctane	–	1.4150
3,3-Dimethylpentane	1.3909	1.3899	2,2,6-Trimethylheptane	1.4077	1.4039
2,3-Dimethylhexane	1.4013	1.4012	2,3,6-Trimethylheptane	1.4130	1.4175
2,4-Dimethylhexane	1.3958	1.3962	2,4,6-Trimethylheptane	–	1.4068
2,5-Dimethylhexane	1.3928	1.3926	3-Ethyloctane	–	1.4154
2,3,3-Trimethylpentane	1.4072	1.4073	2,3,4,5-Tetramethylhexane	–	1.4236
2,3,4-Trimethylpentane	1.4043	1.4037	2,3,4-Trimethyloctane	–	1.4265
2,6-Dimethylheptane	1.4007	1.4006	3,4,5-Trimethyloctane	–	1.4292
2,2,3-Trimethylhexane	1.4100	1.4117	2,3,4,5-Tetramethylheptane	–	1.4322
2,2,3,3-Tetramethylpentane	–	1.4228			
2,2,4,4-Tetramethylpentane	1.4059	1.3958			
2-Methylnonane	1.4099	1.4089			

Analysis of the data in Tables 1 and 2 will yield several conclusions:

1. The numerous experimental figures cited confirm the full serviceability

of our proposed formula and coefficients for calculating the refraction of methane hydrocarbons.

The refraction values computed theoretically practically coincide with those found experimentally.

2. In the transition from one homologue to another in the homologous series of methane hydrocarbons the refraction rises, though not uniformly; the increase in refraction diminishing quite noticeably and regularly, the homologous difference becoming extremely small after C_{15}.

3. A number of empirical rules can be derived from these figures, namely: among the isomeric hydrocarbons, the isomers that have substituents attached to the carbon atom in the 2 position will have the smallest refractive indexes, whereas the isomers with methyl groups closest together along the carbon chain will have the highest refractive indexes. This makes it possible for hydrocarbons with lower molecular weight to have a much higher refractive index than hydrocarbons with higher molecular weights. For example, the octane 2,3,3--trimethylpentane has a higher refractive index than some isomers of nonane (such as 2,6-dimethylheptane) and even higher than some isomers of decane (such as 2,2,4,4-tetramethyldecane).

We are firmly convinced that our proposed formula and coefficients reflect the actual functional relationships between the refraction of organic substances and their molecular structure, at the same time establishing the quantitative aspect of this relationship.

Considering the data of Table 2, we notice a few cases in which the theoretically computed values depart from those found experimentally. We believe that this is due to the fact that the experimental data are not accurate enough. There is no scientific method in contemporary chemical literature for establishing the accuracy of experimental data; that is why quite contradictory figures due to various authors sometimes get into chemical reference works. We believe that the method we have proposed provides the research worker with a scientific method of determining his experimental accuracy; it will make it possible to select the most accurate from among contradictory experimental data, this optimum figure being the one that is closest to the theoretical value computed by our method.

At the same time our method can be employed to compute the refractive indexes of compounds that have not been synthesized as yet; for example, the refractive index of 3-ethyloctane ought to be 1.4154, that of 2,3,4-trimethyl octane 1.4263, etc. (cf. Table 2).

The method we propose has made it possible to set up a theory governing the variation of the refractive index as a function of the molecular structure for the D line of the spectrum with a wavelength of 5390 Å. We have no doubt that our method will also be found adaptable for the analysis and study of the refractive index for other spectrum lines with other wave lengths. Apparently, the general nature of changes in the refractive index as a function of molecular structure will be the same in these other cases as for the D line.

SUMMARY

1. A new method has been proposed for studying the refractive index of

hydrocarbons of the methane series.

2. A new formula has been proposed for computing the refractive indexes of the methane hydrocarbons.

3. The variation of the refractive index with molecular structure has been established quantitatively, and a number of regularities governing its changes in the methane series of hydrocarbons has been found.

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DERIVATIVES OF ACETYLENE

103. MECHANISM OF HYDRATION AND CYCLIZATION OF THE DIENYNES.

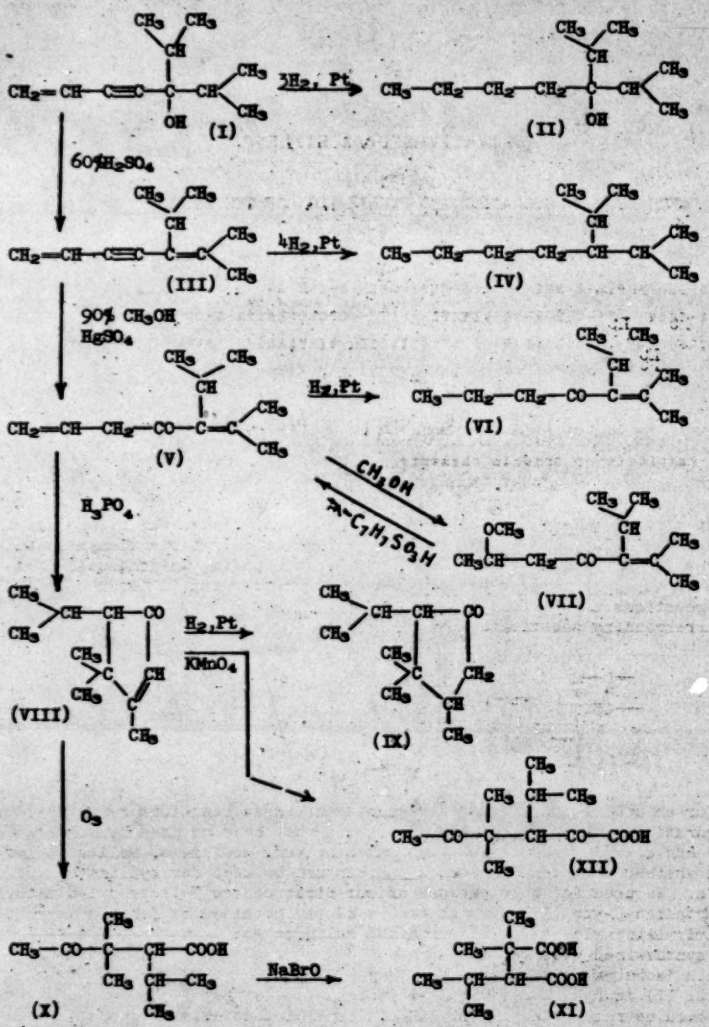
XXI. HYDRATION OF 5-ISOPROPYL-6-METHYL-1,5-HEPTADIEN-3-YNE TO 5-ISOPROPYL-6-METHYL-1,5-HEPTADIEN-4-ONE AND ITS CYCLIZATION TO 1-ISOPROPYL-2,2,3-TRIMETHYL-$\Delta^{3,4}$ - CYCLOPENTEN-3-ONE. A NEW INSTANCE OF CYCLIZATION OF SUBSTITUTED VINYLALLYL KETONES THAT HAVE NO FREE HYDROGEN IN THE VINYL RADICAL

I. I. Nazarov and L. N. Pinkina

Institute of Organic Chemistry of the USSR Academy of Sciences

Up to the present time our laboratory has undertaken the systematic investigation of the hydration and cyclization of only those dienynes that had free hydrogen atoms at the end of the carbon chain, which usually participated in cyclization reactions. As was demonstrated in numerous instances, these reactions always follow the same pattern, resulting in the formation of the corresponding substituted pentenones [1]:

For an understanding of the mechanism of these reactions research into the hydration of 1,1-disubstituted dienynes that have no free hydrogen atoms at the end of the carbon chain would also be very useful, as well as determining whether the dienones formed therein can be used for cyclization reactions. We used for this purpose as our first object 5-isopropyl-6-methyl-1,5-heptadien-3-yne (III), which can be easily obtained by dehydrating diisopropylvinylethynylcarbinol (I) with 60% sulfuric acid, the carbinol in turn being synthesized with a yield of about 80% by the condensation of vinylacetylene with isobutyrone in the presence of powdered sodium hydroxide. When the carbinol (I) is hydrogenated with a Pt catalyst, it absorbs the three hydrogen molecules required by theory and is converted to diisopropylbutylcarbinol (II). In the similar hydrogenation of the dienyne (III) four hydrogen molecules are absorbed and 5-isopropyl-6-methylheptane (IV) is formed. It should be noted that the first three molecules of hydrogen are added to the dienyne (III) very easily, whereas the fourth molecule, representing the hydrogenation of the substituted double bond, is added with great difficulty, the hydrogenation rate dropping about 20 times for this operation. The dienyne (III), like



other unsymmetrically substituted dienynes, is hydrated very easily to 5-isopropyl-6-methyl-1,5-heptadien-4-one (V) by heating in aqueous solutions of methanol in the presence of sulfuric acid and mercury sulfate; when (V) is hydrogenated with a Pt catalyst, only one hydrogen molecule is added to the

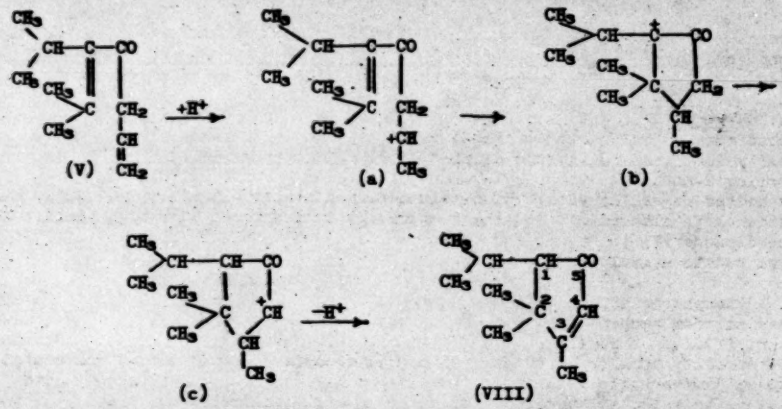
allyl radical, and it is converted into 5-isopropyl-6-methyl-5-hepten-4-one (VI). The structure of the ketone (VI) was confirmed by oxidation with permanganate, yielding acetone and butyric and isobutyric acids. The second double bond in the dienone (V) cannot be hydrogenated under ordinary conditions in the presence of a Pt catalyst, even in a solution of glacial acetic acid, owing to the influence of a large number of substituents and of the high degree of branching of the molecule with a double bond (spatial impediment) upon the hydrogenation process. As has already been said, it is very hard to hydrogenate this double bond, even in the dienyne (III). Hydration of the triple bond of the dienyne (III) is effected in accordance with the rule previously established in our laboratory, specifying that unsymmetrically substituted dienynes added water in such a way that the oxygen is attached solely to the hydrogen linked to the substituted vinyl radical. The dienone (V), like other similar dienones, easily adds methanol to the allyl radical in the presence of mercury sulfate, forming 2-methoxy-5-isopropyl-6-methyl-5-hepten-4-one (VII); when the latter is heated carefully with 0.5% p-toluenesulfonic acid (15 min., 120-130°), the methanol is cleaved off and the dienone (V) is recovered with high yield. When the dienone (V) is heated for a longer time with p-toluenesulfonic acid, it is cyclized to a cyclopentenone (VIII).

Phosphoric acid (sp. gr. 1.76) cyclizes the dienone (V) extremely easily, even at room temperature, into 1-isopropyl-2,2,3-trimethyl-$\Delta^{3,4}$-cyclopenten-5-one (VIII). This same cyclopentenone (VIII) is formed with a yield of some 90% directly from the carbinol (I) or the dienyne (III) when they are heated (60-65°) with phosphoric acid. Thus, when the carbinol (I) is heated with phosphoric acid, all three reactions occur simultaneously: dehydration of the carbinol to the dienyne (III), hydration of this dienyne to the dienone (V), and cyclization of the latter to the cyclopentenone (VIII). Many other tertiary vinylethynylcarbinols undergo similar conversions into cyclopentenones.

The cyclopentenone (VIII), like other cyclopentenones that have but one substituent at the double bond, is easily and smoothly hydrogenated in the presence of a Pt catalyst in a solution of alcohol or of glacial acetic acid, absorbing one molecule of hydrogen and forming 1-isopropyl-2,2,3-trimethylcyclopentan-5-one (IX). The structure of the cyclopentenone (VIII) was finally established by ozonization and oxidation by permanganate.

Ozonization of the cyclopentenone (VIII) yields formic acid and α-isopropyl-β,β'-dimethyllevulinic acid (X), which is smoothly converted into the well-known dimethylisopropylsuccinic acid (XI) by oxidation by a bromine base. Oxidation of the cyclopentenone (VIII) by permanganate produced a high yield of two isomeric acids, $C_{11}H_{18}O_4$, which are in all probability diketo acids (XII), in addition to small quantities of acetone and isobutyrone. Consequently, oxidation of the cyclopentenone (VIII) by permanganate preserves the carbon skeleton. It is not impossible, however, that this may entail molecular rearrangements, such as are observed, for instance, in the oxidation of triisobutylene [3]. The cyclization of the dienone (V) to the cyclopentenone (VIII), which takes place with astonishing ease, indicates that the cyclization reactions of the dienones (substituted vinylallyl ketones) into cyclopentenones by no means require the presence of free hydrogen at the vinyl radical, the absence of this hydrogen not interfering with the cyclization reaction at all. In this case, the cyclization of substituted vinylallyl ketones takes place at the expense of the free hydrogen atoms of the allyl radical, leading to the formation of cyclopentenones with the double bond in a different position ($\Delta^{3,4}$-cyclopenten-5-ones instead of $\Delta^{1,2}$-cyclopenten-5-ones). The cyclization of

the dienone (V), like that of other vinylallyl ketones, is effected not only by phosphoric acid, but by other acids as well (hydrochloric, sulfuric, and p-toluenesulfonic acids). The hydrogen ion is doubtless the initiator of this cyclization, and the following diagram is the most probable mechanism for the latter, as was previously set forth by one of the present authors [4]:



The addition of a hydrogen ion to the dienone (V) yields an unsaturated ion (a), which is cyclized to the cyclic ion (b), which is then isomerized to the cyclic ion(c), the latter being stabilized, with the loss of a proton, as cyclopentenone (VIII).

EXPERIMENTAL

Condensation of Isobutyrone With Vinylallyl Ketone

Into a three-necked round-bottomed flask, fitted with a mechanical stirrer, a dropping funnel, and a thermometer, there were placed 132 g of powdered potassium hydroxide and 270 ml of anhydrous ether, containing 50 g of vinylacetylene. Then a solution of 180 g of isobutyrone (b.p. 124-125°) and 115 g of vinyl acetylene in 480 ml of anhydrous ether are added from the dropping funnel with constant stirring and chilling with a mixture of ice and salt (-5°), during the course of two hours. The reaction mass is stirred in the cold for 5 hours, set aside overnight, and the next day again stirred at room temperature for 5 hours. The potassium hydroxide is carefully washed with water (150 ml), the aqueous layer extracted with ether, the combined ether extract washed with 8% hydrochloric acid (60 ml) and dried with sodium sulfate, the ether driven off over a water bath, and the residue fractionated in vacuo in the presence of pyrogallol. We recovered 30 g of unreacted isobutyrone and 170 g of diisopropylvinylethnylcarbinol (I) as a colorless, transparent, mobile liquid with a characteristic odor, which polymerizes and turns yellow upon standing.

B.p. 78° at 9 mm; n_D^{20} 1.4778; d_4^{20} 0.8859; MR_D found 53.02; calculated 52.05.

5.295 mg substance: 15.410 mg CO_2; 5.143 mg H_2O.
Found %: C 79.42; H 10.87.
$C_{11}H_{18}O$. Calculated %: C 79.45; H 10.91.

Hydrogenation of Diisopropylvinylethnynlcarbinol

10 g of the carbinol (I) dissolved in 30 ml of glacial acetic acid was hydrogenated in the presence of platinum oxide. It absorbed 4.25 liters of hydrogen, the amount required theoretically being 4.4 liters of hydrogen. After hydrogenation was completed, the catalyst was filtered out, the acetic acid was neutralized with a 25% solution of sodium hydroxide, and the product was extracted with ether, dried with sodium sulfate, and fractionated in vacuo. Yield: 9 g of butyldiisopropylcarbinol (II) as a colorless liquid with a specific odor.

B.p. 85° at 10 mm; n_D^{20} 1.4455; d_4^{20} 0.8490; MR_D found 54.42; calculated 54.52.

10.31 mg substance: 28.91 mg CO_2; 12.84 mg H_2O.
10.72 mg substance: 29.98 mg CO_2; 13.18 mg H_2O.
Found %: C 76.55, 76.32; H 13.94, 13.76.
$C_{11}H_{24}O$. Calculated %: C 76.74; H 13.95.

According to the literature, the constants of butyldiisopropylcarbinol are as follows: b.p. 115-118° at 40 mm; n_D^{20} 1.4435; d_4^{20} 0.8487 [5].

When vinylethynyldiisopropylcarbinol dissolved in alcohol is hydrogenated, butyldiisopropylcarbinol is synthesized, with the same constants as when hydrogenated in acetic acid.

Dehydration of Diisopropylvinylethynylcarbinol

A mixture of 50 g of the carbinol (I) and 50 g of 60% sulfuric acid were vigorously stirred for 40 minutes at 60°. The product was extracted with ether, washed with a solution of soda, dried with sodium sulfate, and fractionated in vacuo after the ether had been driven off. 35.5 g of 6-methyl-isopropyl-1,5-heptadien-3-yne (III) was obtained as a colorless liquid with a characteristic odor that yellows rapidly upon standing.

B.p. 64-65° at 15 mm; n_D^{20} 1.5010; d_4^{20} 0.8210; MR_D found 53.11; calcu. 50.06.

3.530 mg substance: 11.510 mg CO_2; 3.516 mg H_2O.
5.338 mg substance: 17.430 mg CO_2; 5.235 mg H_2O.
Found %: C 88.99, 89.11; H 11.14, 10.97.
$C_{11}H_{18}$. Calculated %: C 89.11; H 10.89.

In addition, we obtained 2.5 g of 2,2,3-trimethyl-1-isopropyl-$\Delta^{3,4}$-cyclopenten-5-one (V), described below, with a b.p. of 95-97° at 10 mm; n_D^{20} 1.4765.

Its semicarbazone fused at 199° (from alcohol); a mixed sample with the semicarbazone of the product of cyclohydration of the dienyne gave no depression.

Hydrogenation of 6-Methyl-5-isopropyl-1,5-heptadien-3-yne

10 g of the dienyne (III) dissolved in 40 ml of glacial acetic acid was

hydrogenated in the presence of platinum oxide. A total of 6200 ml of hydrogen was absorbed, 4735 ml, or 3 molecules, being absorbed during the first 2.5 hours. Subsequent hydrogenation was slow, 18 hours being required for the absorption of the remaining 1465 ml of hydrogen, though fresh portions of catalyst were added three times. Theoretically, 6050 ml of hydrogen are required for the hydrogenation of two double bonds and one triple bond.

The catalyst was filtered out, the acetic acid neutralized with a 25% solution of sodium hydroxide, and the product extracted with ether, dried with sodium sulfate, and fractionated in vacuo over metallic sodium after the ether had been driven off. Yield: 8.4 g of 6-methyl-5-isopropylheptane (IV) as a colorless, transparent liquid with an agreeable odor.

B.p. 51.5-52° at 9 mm and 172-173° at standard pressure; n_D^{20} 1.4232; d_4^{20} 0.7565; MR_D found 52.53; calculated 52.99.

3.286 mg substance: 10.171 mg CO_2; 4.531 mg H_2O.
3.182 mg substance: 9.862 mg CO_2; 4.385 mg H_2O.
Found %: C 84.47, 84.65; H 15.60, 15.42.
$C_{11}H_{24}$. Calculated %: C 84.61; H 15.39.

According to the literature, the constants of 6-methyl-5-isopropylheptane are: b.p. 182°; n_D^{20} 1.4265 d_4^{20} 0.7603. [8].

Cyclohydration of 6-Methyl-5-isopropyl-1,5-heptadien-3-yne

A mixture of 7.4 g of the dienyne (III) and 7.5 ml of phosphoric acid (sp. gr. 1.76) was stirred for 7 hours at 60-65°. The product was diluted with water, extracted with ether, washed with a solution of soda, dried with sodium sulfate, and fractionated in vacuo. Yield: 6.6 g of 2,2,3-trimethyl-1-isopropyl-$\Delta^{3,4}$-cyclopenten-5-one (VIII) as a colorless, transparent liquid with a characteristic camphor smell.

B.p. 100° at 10 mm; n_D^{20} 1.4778; d_4^{20} 0.9205; MR_D found 50.71; calcul. 50.34.

5.380 mg substance: 15.603 mg CO_2; 5.229 mg H_2O.
Found %: C 79.14; H 10.87.
$C_{11}H_{18}O$. Calculated %: C 79.45; H 10.91.

Its semicarbazone fused at 201.5° (from alcohol).

3.805 mg substance: 0.605 ml N_2(23°, 775 mm).
3.340 mg substance: 0.529 ml N_2(22°, 746 mm).
Found %: N 18.70, 18.72.
$C_{12}H_{21}ON_3$. Calculated %: N 18.83.

The 2,4-dinitrophenylhydrazone of this cyclopentenone (VIII) fused at 128° (from alcohol).

Hydrogenation of 2,2,3-Trimethyl-1-isopropyl-$\Delta^{3,4}$-cyclopenten-5-one

4.9 g of the substance (VIII) dissolved in 20 ml of glacial acetic acid was hydrogenated in the presence of platinum oxide. It absorbed 786 ml. of hydrogen; theoretically the hydrogenation of one double bond requiring 742 ml of hydrogen.

The catalyst was filtered out, the acetic acid neutralized with a 10% solution of sodium hydroxide, and the product extracted with ether, dried with sodium sulfate, and fractionated in vacuo after the ether had been driven off. Yield: 4 g of 2,2,3-trimethyl-1-isopropylcyclopentan-5-one (IX) as a colorless, transparent liquid with a characteristic turpentine odor.

B.p. 78-80° at 7.5 mm and 209-212° at standard pressure; n_D^{20} 1.4548; d_4^{20} 0.9026; MR_D found 50.50; calculated 50.80.

The semicarbazone of this ketone fused at 180.5° (from methanol).

4.100 mg substance: 0.650 ml N_2 (22°, 774 mm).
3.720 mg substance: 0.610 ml N_2 (21°, 767 mm).
Found %: N 18.68, 18.50.
$C_{12}H_{23}ON_3$. Calculated %: N 18.50.

2,2,3-Trimethyl-1-isopropyl-$\Delta^{3,4}$-cyclopenten-5-one likewise hydrogenates easily when dissolved in methanol, absorbing one molecule of hydrogen and yielding a substance with the same constants as when hydrogenated in acetic acid.

Its semicarbazone also fuses at 180°, and a mixed sample with the semicarbazone of the product of hydrogenation in acetic acid causes no depression.

Ozonization of 2,2,3-Trimethyl-1-isopropyl-$\Delta^{3,4}$-cyclopenten-5-one

Ozonized oxygen was passed through a solution of 25.4 g of substance (VIII) in 40 ml of anhydrous chloroform for 45 hours at the rate of 4 liters per hour (ozone concentration 6%).

The solution of the ozonide was poured into 40 ml of water and stirred for 2 hours at room temperature and 10 hours at 60°. After neutralization with soda, the alkaline aqueous solution was extracted with ether to leach out the neutral products of ozonization. Since 17.5 g of "neutral products" remained, after the solution had been driven off, as a yellow oil that exhibited an acid litmus reaction, the whole mass was subjected to two more heatings (60°) with a 10% solution of soda (20 g) for 14 hours with vigorous stirring. The aqueous extract, which gave an alkaline reaction with litmus paper, was extracted with ether; after the solvent had been driven off from the ether extract, we had left 3 g in all of a substance that exhibited an acid reaction to litmus paper. Fractionation of the latter in vacuo isolated 0.2 g of isobutyrone (b.p. 69° at 100 mm) and 2 g of a partially crystallizing mixture of the neutral products with α-isopropyl-β,β-dimethyllevulinic acid. B.p. 100-121° at 2.5 mm; n_D^{20} 1.4642.

A sample taken from the aqueous solutions, indicated 3.4 g of formic acid (48% of the theoretical) by the calomel method, when recomputed in terms of the aggregate volume.

The aqueous solution of the salts was evaporated to dryness, the salts treated with concentrated hydrochloric acid, and the organic acids carefully extracted with ether and dried with sodium sulfate.

After the ether had been driven off over a water bath, 3.1 g of formic acid boiling at 101-109° at normal pressure, was driven off in vacuum (10 mm).

A test sample with arsenous oxide to produce a cacodyl compound also exhibited the presence of acetic acid.

The 16.7 g of partially crystallized residue of the organic acids was distilled in an oil-pump vacuum. We obtained 11 g of a highly viscous yellowish liquid with an agreeable odor reminding one of honey; b.p. 118-119° at 2.5 mm; n_D^{27} 1.4579. The substance crystallized in part upon standing and freezing for several days. The snow-white crystals, after filtering out, washing with alcohol, and drying in an exsiccator, fused at 48°; they were α-isopropyl-β,β-dimethyllevulinic acid (X) (yield about 3 g).

0.10713 g substance: 5.65 ml 0.1N KOH.
Found: M 189.6.
$C_{10}H_{18}O_3$. Calculated: M 186.
3.255 mg substance : 7.685 mg CO_2; 2.861 mg H_2O.
3.100 mg substance : 7.317 mg CO_2; 2.720 mg H_2O.
Found %: C 64.45, 64.46; H 9.83, 9.82.
$C_{10}H_{18}O_3$. Calculated %: C 64.51; H 9.68.

The semicarbazone fuses at 182° (from alcohol).

3.310 mg substance: 0.517 ml N_2 (24°, 740 mm).
3.280 mg substance: 0.507 ml N_2 (23°, 750 mm).
Found %: N 17.49, 17.59.
$C_{11}H_{21}O_3N_3$ Calculated %: N 17.28.

The 2,4-dinitrophenylhydrazone fuses at 172-173° (from alcohol).

Oxidation of α-Isopropyl-β,β-dimethyllevulinic Acid by a Bromine Base.

To a solution of 0.7 g of sodium hydroxide in 7 ml of water there was added 0.36 g of acid (X), after which 1.1 g of bromine was added drop by drop, the whole being constantly stirred and chilled with ice water. After 3.5 hours of stirring the odor of bromoform was noticed, the latter separating out in oily drops. The water and the bromoform were driven off under slight vacuum, the distillate extracted with ether, and the ether extract dried with sodium sulfate. After the ether had been driven off there remained about 0.1 g of a yellow oil with the characteristic odor of bromoform: it could not be redistilled because of its small quantity.

The salt residue was treated with concentrated hydrochloric acid (10 ml), the organic acid extracted with ether, and the ether extract washed with a 1% solution of hyposulfite to remove the traces of bromine and then dried with sodium sulfate. After the ether had been driven off, the almost completely crystallized residue was twice recrystallized from water. We obtained 0.3 g of α-isopropyl-β,β-dimethylsuccinic acid (XI) with a b.p. of 135°.

4.196 mg substance: 4.5 ml 0.01N NaOH.
Found: M 186.5.
$C_9H_{16}O_4$. Calculated: M 188.
4.630 mg substance: 9.764 mg CO_2; 3.530 mg H_2O.
6.265 mg substance: 13.167 mg CO_2; 4.940 mg H_2O.
Found %: C 57.55, 57.35; H 8.53, 8.64.
$C_9H_{16}O_4$. Calculated %: C 57.45; H 8.51.

According to the literature, dimethylsuccinic acid fuses at 141-142° [2].

Oxidation of 2,2,3-Trimethyl-1-isopropyl-$\Delta^{3,4}$-cyclopenten-5-one

To a mixture of 20 g of substance (VIII) and 700 ml of water, constantly stirred and chilled, 48 g of powdered permanganate was added in small batches during the course of 6 hours. The manganese dioxide was filtered out and washed several times, first with cold water and then with hot. 0.3 g of acetone, b.p. 56-70° (whose p-nitrophenylhydrazone fused at 148° and did not cause a depression when mixed with a known sample) was isolated from the aqueous solution by distillation, impregnation of the distillate with potash, extraction with ether, and subsequent fractionation. In addition to acetone, 1 g of isobutyrone, b.p. 120-128°, was also isolated from the neutral products; its semicarbazone fused at 153-154° and did not cause a depression when mixed with a standard sample.

The aqueous solution of the salts of the organic acids was evaporated to dryness, the salts were treated with concentrated hydrochloric acid (45 ml), and the organic acids were extracted with ether and dried by sodium sulfate. After the ether had been driven off over a water bath, a few drops of formic acid were distilled off in a 100 mm vacuum. The brown oily residue of organic acids (14 g) crystallized. The crystals were filtered out (8.5 g) and washed with carbon tetrachloride; after repeated fractional crystallization from a mixture of ether and carbon tetrachloride we isolated two isomeric 3,3-dimethyl-4-isopropyl-α-δ-caproic acids (XII). The first isomer has a b.p. of 144°.

0.1655 g substance: 7.58 ml 0.1N KOH.
Found: M 218.
$C_{11}H_{18}O_4$. Calculated: M 214.

4.050 mg substance: 9.200 mg CO_2; 3.080 mg H_2O.
4.040 mg substance: 9.150 mg CO_2; 3.052 mg H_2O.
Found %: C 61.99, 61.81; H 8.51, 8.45.
$C_{11}H_{18}O_4$. Calculated %: C 61.88; H 8.41.

The second isomer has a b.p. of 112-114°.

0.0995 g substance: 4.73 ml 0.1N KOH.
Found: M 211.
$C_{11}H_{18}O_4$. Calculated : M 214.
6.090 mg substance: 13.657 mg CO_2; 4.560 mg H_2O.
3.680 mg substance: 12.720 mg CO_2; 4.310 mg H_2O.
Found %: C 61.20, 61.12; H 8.38, 8.49.
$C_{11}H_{18}O_4$. Calculated %: C 61.68; H 8.41.

Hydration of 6-Methyl-5-isopropyl-1,5-heptadien-3-yne

a) A mixture of 180 ml of 90% methanol, 0.4 ml of concentrated sulfuric acid, 3 g of mercury sulfide, and 40 g of the dienyne (III) was stirred for 90 min. at 60°. During this time another 3 g of mercury sulfate was added in 1-gram batches. The reaction mixture was diluted with water and treated with ether; the ether extract was washed with water and dried with sodium sulfate; after the ether had been driven off, the residue was fractionated in vacuo. The following fractions were obtained:

I. B.p. 74-81° at 20 mm; n_D^{20} 1.4890 – 2.8 g;

II. B.p. 81-89° at 20 mm; n_D^{20} 1.4982 – 7.6 g;

III. B.p. 89-102°, 20 mm; n_D^{20} 1.4742 – 28.7 g.

Repeated distillation yielded, together with the intermediate fractions, 9 g of the initial dienyne (b.p. 63-65° at 10 mm; n_D^{20} 1.5016) and 8.5 g of 5-isopropyl-6-methyl-1,5-heptadien-4-one (V).

B.p. 88-88.5° at 10 mm; n_D^{20} 1.4728; d_4^{20} 0.8816; MR_D found 52.80; calculated 52.07

6.344 mg substance: 18.428 mg CO_2; 6.182 mg H_2O.
Found %: C 79.27; H 10.90.
$C_{11}H_{18}O$. Calculated %: C 79.45; H 10.91.

Its semicarbazone fused at 120-121° (from alcohol).

3.765 mg substance: 0.640 ml N_2 (21°, 736 mm).
5.005 mg substance: 0.845 ml N_2 (21°, 732 mm).
Found %: N 19.11, 18.88.
$C_{12}H_{21}N_3O$. Calculated %: N 18.83.

Moreover, this experiment also yielded 2.5 g of the 2-methoxy-5-isopropyl-6-methyl-5-hepten-4-one (VII) described below. B.p. 101° at 10 mm; n_D^{20} 1.4558.

When the time during which the reagents were heated was increased to five hours, no more of the initial dienyne was recovered, and the principal reaction product was the methoxy ketone (VII) with a trace of the dienone (V). One of these runs is described below.

b) A mixture of 25 g of the dienyne (III), 110 g of 90% methanol, 0.25 ml of concentrated sulfuric acid, and 2 g of mercury sulfate was mixed for 5 hours at 50°. During this time another 2 g of mercury sulfate was added in small batches. Treatment like that described in the preceding experiment yielded 3 g of the dienone (V), b.p. 82-85° at 8 mm; n_D^{20} 1.4720, and 25 g of the methoxy ketone (VII).

B.p. 96-98° at 8 mm; n_D^{20} 1.4558; d_4^{20} 0.9134; MR_D found 59.01; calc. 58.80.

4.260 mg substance: 11.409 mg CO_2; 4.185 mg H_2O.
Found %: C 72.99; H 10.99.
$C_{12}H_{22}O_2$. Calculated %: C 72.72; H 11.11.

Heating the methoxy ketone (VII) with 0.5% p-toluenesulfonic acid caused methanol to split off, and the dienone (V) was recovered.

Splitting off Methanol from the Methoxy Ketone (VII)

10 g of the methoxy ketone was heated for 15 minutes with 0.5% p-toluenesulfonic acid in a 80-mm vacuum, the bath temperature being 130°. At the end of this time the mixture was poured into 20 ml of a 10% soda solution and vigorously shaken in a separatory funnel to neutralize the p-toluenesulfonic acid. The product was extracted with ether, dried with potash, and -- after the ether had been driven off – fractionated in vacuum. Yield: 5.4 g of 5-isopropyl-6-methyl-1,5-heptadien-4-one (V).

B.p. 53.5-55° at 2 mm; n_D^{20} 1.4732; d_4^{20} 0.8824; MR_D found 52.80; calc. 52.08.

Its semicarbazone fused at 120-121°, and a mixed sample with the semicarbazone of the dienone (V) described above, synthesized by the direct hydration of the dienyne (III), caused no depression.

If the methoxy ketone is distilled in vacuum with p-toluenesulfonic acid, and distillation is not stopped after the methanol is split off, we get, together with the dienone, some of the cyclic ketone (VIII), identified by means of its semicarbazone.

12.7 g of the methoxy ketone (VII) was distilled with 0.5% p-toluenesulfonic acid in an oil-pump vacuum. We obtained 4.4 g of the 6-methyl-5-isopropyl-1,5-heptadien-4-one described above, as a mobile yellow liquid with a specific odor. B.p. 80-83° at 8.5 mm; n_D^{20} 1.4732; d_4^{20} 0.8834. In addition, 2.1 g of the cyclopentenone (VIII) was recovered as a colorless, transparent liquid with the characteristic odor of camphor; b.p. 89-92° at 8.5 mm; n_D^{20} 1.4762; its semicarbazone fused at 199° (from alcohol) and caused no depression with the sample described above.

Hydrogenation of 6-Methyl-5-isopropyl-1,5-heptadien-4-one

3 g of the dienone (V) dissolved in 35 ml of methanol was hydrogenated in the presence of platinum oxide. In 30 minutes 435 ml of hydrogen was absorbed, and hydrogenation was stopped. Theoretically, 440 ml of hydrogen is required for the hydrogenation of one double bond.

The catalyst was filtered out, the methanol driven off over a water bath, and the residue fractionated in vacuum. We obtained 2.3 g of 6-methyl-5-isopropyl-5-hepten-4-one (VI) as a colorless, transparent liquid with a characteristic odor.

B.p. 76-77° at 9 mm; n_D^{20} 1.4456; d_4^{20} 0.8539; MR_D found 52.43; calc. 52.54.

3.782 mg substance: 10.855 mg CO_2; 4.089 mg H_2O.
6.378 mg substance: 18.315 mg CO_2; 6.924 mg H_2O.
Found %: C 78.33; 78.37; H 12.10, 12.15.
$C_{11}H_{20}O$. Calculated %: C 78.57; H 11.90.

We were unable to obtain the corresponding crystalline derivatives by letting the product react with semicarbazide and 2,4-dinitrophenylhydrazine. Nor were we able to obtain a fully hydrogenated dienone by hydrogenation in acetic acid.

Oxidation of 6-Methyl-5-Isopropyl-5-hepten-4-one

To 9.8 g of substance (VI) and 325 ml of water, constantly stirred and chilled, 25 g of powdered permanganate was added in small batches during 10 hours. The precipitate of manganese dioxide was filtered out and washed repeatedly with hot water. The wash waters were combined with the original filtrate. Distillation, saturation of the distillate with potash, and subsequent distillation (these operations were repeated three times) yielded 1.1 g of acetone, b.p. 58-90°, whose p-nitrophenylhydrazone fused at 147° and did not cause a depression with a known sample. Moreover, from the neutral products we isolated 1 g of a substance with a b.p. of 62-71° at 15 mm; n_D^{20} 1.4242; with

the odor of isobutyrone, but its semicarbazone fused at 167° (instead of 153°, the m.p. of isobutyrone).

The aqueous solution of the salts was evaporated to dryness, the salts decomposed by concentrated hydrochloric acid, and the acids carefully extracted with ether, dried with sodium sulfate, and – after the ether had been driven off – fractionated, at first in vacuo and then at standard pressure. Yield: 5 g of a mixture of butyric and isobutyric acids, b.p. 147-163°.

0.7003 g substance: 7.98 ml 1.0N KOH.
Found: M 87.6.
$C_4H_8O_2$. Calculated: M 88.0.
0.1715 g substance: 0.0949 g Ag;
Found %: Ag 55.62.
$C_4H_7O_2Ag$. Calculated %: Ag 55.34.

Cyclization of 6-Methyl-5-isopropyl-1,5-heptadien-4-one

a) A mixture of 2.6 g of the dienone (V) and 3 ml of phosphoric acid (sp. gr. 1.76) was stirred for 6 hours at 60-65°. The reaction mass was diluted with water, and the product extracted with ether, dried with sodium sulfate, and distilled in vacuo. Yield: 2.1 g of 2,2,3-trimethyl-1-isopropyl-$\Delta^{3,4}$-cyclopenten-5-one (VIII) as a colorless liquid with the characteristic odor of camphor. B.p. 92-93° at 8 mm; n_D^{20} 1.4780. Its semicarbazone fused at 200.5°, and a mixed sample with the semicarbazone of the product of the cyclohydration of the dienyne (III) caused no depression.

b) A mixture of 3 g of the dienone (V) and 3 ml of phosphoric acid (sp. gr. 1.76) was stirred for 5 hours at 20°. After the usual treatment and vacuum distillation we obtained 2.2 g of the cyclopentenone (VIII) with the characteristic odor of camphor. B.p. 105-106.5° at 14 mm; n_D^{20} 1.4756.

Its semicarbazone also fused at 200.5° (from alcohol) and caused no depression with the samples described above.

Synthesis of 2,2,3-Trimethyl-1-isopropyl-$\Delta^{3,4}$-cyclopenten-5-one from Diisopropylvinylethynylcarbinol

To 100 g of the carbinol (I) 100 ml of phosphoric acid (sp. gr 1.76) was added, drop by drop, with vigorous stirring and chilling with ice water; this caused the the temperature of the reaction mass to rise from 10 to 15°. Then stirring was continued for 6 hours at 60-65°. During the course of 1 hour the temperature in the flask rose to 88° (with the bath temperature at 63°), and the characteristic camphor odor of the cyclic ketone, (VIII) made its appearance. After the reaction was over, the mixture was diluted with water, and the product extracted with ether, dried with sodium sulfate, and distilled in vacuum. Yield: 84 g of the cyclopentenone (VIII), b.p. 92-95° at 8 mm; n_D^{20} 1.4770. Its semicarbazone fused at 200° (from alcohol), and a mixed sample with the semicarbazone of the dienyne cyclohydration product caused no depression.

SUMMARY

Condensation of isobutyrone with vinylacetylene results in the formation, with high yield, of diisopropylvinylethynylcarbinol (I), which is easily

dehydrated to 5-isopropyl-6-methyl-1,5-heptadien-3-yne (III) by dilute sulfuric acid. When the dienyne (III) is heated in aqueous solutions of methanol in the presence of sulfuric acid and mercury sulfate, the dienone (V) is easily formed, the latter, in turn, being cyclized to the cyclopentenone (VIII) with extreme ease by the action of acids (phosphoric, sulfuric, hydrochloric, and p-toluene-sulfonic acids). With phosphoric acid, the cyclization of the dienone (V) takes place quantitatively at room temperature. This cyclization is a new typical example of cyclization of the vinylallyl ketones that have no free hydrogen in the vinyl radical, and that is why it is effected at the expense of the hydrogen atoms of the allyl group.

An ion mechanism is proposed to explain this cyclization reaction.

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ALLYL REARRANGEMENTS

XII. ACTION OF ORGANOMAGNESIUM COMPOUNDS AND OF MAGNESIUM UPON ISOMERIC ETHOXY- AND BUTOXYCHLOROPENTENES

A. N. Pudovik and G. M. Vinokurova

Laboratory of Organic Chemistry of the Kazan State University

Chemists first encountered allyl rearangements at the end of the last century. Lvov [1] and Sheshukov [2], studying the action of chlorine upon isobutylene in Butlerov's laboratory, and the properties of the products they obtained, came close to a study of these rearrangements. The isomeric transformations of the unsaturated terpene alcohols: linalool and geraniol, were discovered somewhat later [3]. Allyl rearrangements were subsequently investigated by Claisen [4], Prevost [5], Kirrman [6], Meisenheimer and Link [7], Tishchenko [8], Ingold and Burton [9], Heilbron, Jones, and assoc. [10], Nazarov and assoc. [11], Zalkind and Kulikov [12], Young and assoc. [13], and in a number of other research papers [14]. Parallel with this study of allyl rearrangements, several endeavors were made to elucidate their mechanism. Among the first of these were the ideas put forward by Tiemann [15] and Meisenheimer [16], which did not obtain wide acceptance, however. Much more promising seemed to be Prevost's "synicnium" theory [17] based upon electronic notions. Employing the concept of the complete ionization of the halogen atom or of any other group as the anion with simultaneous breaking of the double bond and the formation of a tripolar ion, Prevost concluded that the results of the reaction need not depend upon the initial position of the liberated group or on the nature of the reagent cation. The researches of Meisenheimer and Link [7], Tischenko [8], Young and assoc. [13], and Pudovik and Arbuzov [14], however, disclosed the incorrectness of Prevost's theory as well as of its experimental foundations. It was demonstrated by Young and his associates, as well as by the present authors, that the reactions between the halogen allyl isomers and metal acetates, in an aqueous and alcoholic base, previously investigated by Prevost, are not of the ionic type, but are mixed ionic-molecular in nature.

As for the reactions of organomagnesium compounds with halogen allyl isomers, practically no work has been done in this field since Prevost and Kirrman. Prevost explained the mechanism of these reactions, by analogy with other reactions of halogen allyl isomers, on the basis of his "synionium" theory, although there was no adequate experimental basis for the same, since in most instances the investigation of these reactions was of a one sided nature; the reactions were usually carried out with one of the halogen allyl isomers.

Recently, Henne and Turk [18], as well as one of the present authors and Arbuzov [19], have demonstrated – using as an example the reactions of isomeric

methoxychloropentenes with benzenemagnesium bromide – that these reactions result in the formation of identical mixtures of isomeric hydrocarbons, consisting of 40-44% of 1-methoxy-5-phenylpentene-3 and 20-22% of 1-methoxy-5-phenyl-pentene-4. The results obtained led us to conclude that these reactions were "ionic". To pursue this study further and to confirm the suggested mechanism of these reactions, we have investigated in the present paper some other reactions between Grignard compounds, containing aliphatic and aromatic radicals, and isomeric ethoxy and butoxychloropentenes.

The reactions were carried out in the usual manner in an ether solution. The reactions between ethyl-, butyl- and phenylmagnesium bromides and the isomeric ethoxy- and butoxychloropentenes yielded in each case only one of the expected isomeric alkoxy alkylpentenes, with structures corresponding to the initial chlorides. The product yields were 60-80%. The constants of the products obtained are listed in the table below.

Test No.	Formula	Boiling point	n_D^{20}	d_4^{20}
1	$C_2H_5OCH_2CH_2CH{=}CHCH_2CH_2CH_3$.....	59-61° (13 mm)	1.4205	0.8022
2	$C_2H_5OCH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_3$.....	86-88° (10 mm)	1.4280	0.8052
3	$n\text{-}C_4H_9OCH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_3$...	109-110° (10 mm)	1.4340	0.8147

The structure of one of the products – 1-ethoxyheptene-3 — was confirmed by oxidation with potassium permanganate. Ethoxypropionic and butyric acids were obtained. It may be concluded from these results that, as in the reaction between isomeric methoxychloropentenes and phenylmagnesium bromide previously investigated by us, the reactions are of the "ionic" type, forming a resonant carbon ion as follows:

$$\left.\begin{matrix}ROCH_2CH_2CH{=}CHCH_2Cl\\ ROCH_2CH_2CHClCH{=}CH_2\end{matrix}\right\} \rightarrow \left[\begin{matrix}ROCH_2CH_2CH{=}\overset{+}{C}H{-}CH_2\\ ROCH_2\overset{+}{C}H_2CH{-}CH{=}CH_2\end{matrix}\right] + Cl^- + R'MgBr \longrightarrow$$

$$\longrightarrow ROCH_2CH_2CH{=}CHCH_2R'.$$

The formation of only one of the possible isomeric hydrocarbons, corresponding in structure to the initial chloride, may be due chiefly the the circumstance that the $C_2H_5OCH_2CH_2$— and $C_4H_9OCH_2CH_2$— groups possess a high inductive effect as compared to $CH_3OCH_2CH_2$—, and as a result the equilibrium between the resonance forms of the ions is shifted entirely toward one of those two. Besides these hydrocarbons, in reactions between isomeric alkoxy chloropentenes and Grignard reagents containing aliphatic radicals, small amounts of high-boiling products corresponding in composition to diethoxy and dibutoxydecadienes were also isolated.

In the reactions between isomeric ethoxychloropentenes and ethylmagnesium bromide and butylmagnesium bromide, a product with a b.p. of 130-133° (11 mm); n_D^{20} 1.4465; d_4^{20} 0.8712, was isolated; with the butoxychloropentenes the product had a b.p. of 171-173° (11 mm); n_D^{20} 1.4510; d_4^{20} 0.8623. The yields of these products averaged 25-30%.

No high-boiling products were found in the reactions with phenylmagnesium bromide.

The formation of dialkoxydecadienes in these reactions apparently is due to an exchange reaction between the halogen allyl compound and the Grignard reagent; it can be represented by the following equations:

$$C_2H_5OCH_2CH_2CH{=}CHCH_2Cl + C_2H_5MgBr \longrightarrow C_2H_5OCH_2CH_2CH{=}CHCH_2MgBr$$

$$C_2H_5OCH_2CH_2CH{=}CHCH_2MgBr + ClCH_2CH{=}CHCH_2CH_2OC_2H_5 \rightarrow C_{14}H_{26}O_2 + MgBrCl$$

To explain the structure and the mechanism of formation of these products, we studied the reactions of isomeric alkoxychloropentenes with magnesium. The reactions were carried out in an ether solution and were activated by the addition of iodine and ethyl bromide. These reactions furnished – with yields of the order of 60-80% – products whose constants are identical with the high-boiling products mentioned above. The substance with a b.p. of 130-133° (11 mm) was oxidized by potassium permanganate; ethoxypropionic acid was isolated and the presence of formic acid was demonstrated. Of the three possible isomers that can be formed when magnesium acts upon the isomeric ethoxypentenes:

1. $C_2H_5OCH_2CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2CH_2OC_2H_5$.

2. $C_2H_5OCH_2CH_2CH{=}CHCH_2\underset{\displaystyle CH{=}CH_2}{CH}CH_2CH_2OC_2H_5$.

3. $C_2H_5OCH_2CH_2\underset{\displaystyle CH{=}CH_2}{CH}\!\!-\!\!-\!\!-\underset{\displaystyle CH{=}CH_2}{CH}CH_2CH_2OC_2H_5$,

ethoxypropionic and formic acids can be simultaneously formed only from the second (primary-secondary) form, which therefore corresponds to the structure of the products we have obtained. The results obtained agree with the data of Henne and Turk [18] and Young, Roberts, and Waks [20], who found that when butene magnesium bromide is reacted with butenyl bromides 50% of the primary-secondary form of dibutenyl is formed, whereas when it is reacted with butenyl chlorides, the yield is as high as 90%.

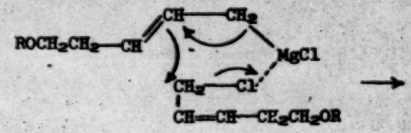
The formation of compounds whose structure corresponds to the secondary form of the Grignard reagent was also observed by Young and his associates [21] in their study of the action of compounds containing a carbonyl group and of phenylacetylene upon halogen allylmagnesium derivatives.

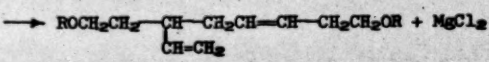
To explain the mechanism of these reactions they assume an abnormal cyclic mechanism, previously proposed by Gilman [22], believing that the reaction takes place with the Grignard reagent in the crotylic form.

As for the mechanism of the reactions we have studied, they (like the reactions with carbonyl compounds already mentioned) cannot be explained by the adopted ionic or ionic-molecular reaction mechanism, since we would then have to expect the formation, in the main, of hydrocarbons with a normal chain (di-primary form), which are not present.

Without foreclosing the question of the structure of the Grignard reagent consisting of allylmagnesium compounds, we think that the reactions we have investigated, by analogy with the reactions of carbonyl compounds, can likewise be explained by means of an abnormal mechanism, involving an electron transposition in the six-membered ring for the primary form of the Grignard reagent, and by a normal mechanism for the secondary form:

(I)





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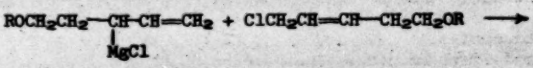

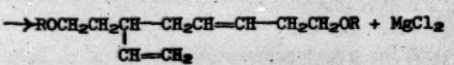

In the secondary chloride, a rearrangement evidently takes place during the reaction into an isomeric chloride, which then reacts in turn with the Grignard reagent in the same manner. The adoption of diagrams to explain the mechanism of these reactions seems to be still somewhat premature, since the problem of the structure of the Grignard reagent consisting of allyl halogen compounds itself is not finally resolved. The analogy cited between the reactions of benzylmagnesium chloride and the Grignard reagent consisting of allyl halogen compounds, which is Young's principal argument in favor of the adoption of the crotylic form, seems to be still not entirely convincing, since benzylmagnesium chloride, in addition to its abnormal reactions, sometimes reacts in the normal manner.

EXPERIMENTAL

Action of Methylmagnesium Bromide on 1-Ethoxy-6-chloropentene-3

Into a round-bottomed flask fitted with a reflux condenser and a dropping funnel there was placed 7.8 g of magnesium chips. The chips were activated by heating with crystalline iodine, after which absolute ether was poured over them. Then a solution of 37 g of ethyl bromide in 100 ml of absolute ether is added to them drop by drop. The violent reaction of formation of a Grignard reagent took place. When the reaction had abated, the reaction mixture was heated for an hour over a water bath, after which 40 g of 1-ethoxy-5-chloropentene-3 was added drop by drop. When the primary chloride was added, no visible changes in the reaction mixture were observed at the very beginning; after heating for an hour over the water bath it began to grow thick, finally solidifying into a jellylike mass. When the reaction was over, the ether was driven off, and the residue treated with cold water and dilute hydrochloric acid while chilled. The ether layer was separated and dried with calcium chloride. The ether was driven off over a water bath, and the residue fractionated in vacuum with a Widmer spiral column.

Several fractionations yielded 7.4 g of the initial chloride, 16.8 g of 1-ethoxyheptene-3, with a b.p. of 59-61 at 13 mm:

d_4^{20} 0.8022; n_D^{20} 1.4205; MR_D 44.85.

$C_9H_{18}OF$. Calculated MR_D 44.93.

0.0903 g substance: 0.2512 g CO_2; 0.1027 g H_2O.
Found %: C 75.86; H 12.63.
$C_9H_{18}O$. Calculated %: C 76.05; H 12.67.

and 7.1 g of 1-ethoxy-6-β-ethoxyethyloctadiene-3,7 with a b.p. of 130-133° at 11 mm:

d_4^{20} 0.8712; n_D^{20} 1.4465; MR_D 69.24.

$C_{14}H_{26}O_2F_2$. Calculated MR_D 69.20.

0.0968 g substance: 0.2623 g CO_2; 0.1005 g H_2O.
Found %: C 74.18; H 11.52.
$C_{14}H_{26}O_2$. Calculated %: C 74.33; H 11.5.

Action of Ethylmagnesium Bromide on 1-Ethoxy-3-chloropentene-4

An ether solution of ethylmagnesium bromide was prepared in the usual manner from 9.1 g of magnesium chips and 41.1 g of ethyl bromide. To this ether solution of the Grignard reagent 40 g of 1-ethoxy-3-chloropentene-4 was added drop by drop, after which the reaction mixture was heated over a water bath for 5 hours. When the reaction was over, the ether was driven off, and the remaining jellylike mass was treated with water and dilute hydrochloric acid. Then the ether layer was separated and dried with calcium chloride; the ether was driven off, and the residue fractionated with a Widmer spiral column. Repeated fractionations yielded 2 g of the initial chloride, 18.9 g of 1-ethoxyheptene-3:

B.p. 159-161° at 760 mm: d_4^{20} 0.8018; n_D^{20} 1.4186;

and 8.2 g of 1-ethoxy-6-β-ethoxyethyloctadiene-3,7:

B.p. 130-134° at 11 mm; d_4^{20} 0.8712; n_D^{20} 1.4465.

Oxidation of 1-Ethoxyheptene-3 by Potassium Permanganate

Into a 1-liter bottle there were poured 620 ml of distilled water and 11.4 g of 1-ethoxyheptene-3. Then 37.1 g of potassium permanganate was poured in in small batches, the bottle being constantly shaken and cooled by running water. The shaking was continued for one hour, after which the mixture was set aside to stand overnight. After the supernatant liquor above the deposit of manganese peroxide had clarified, the latter was filtered out and washed a few times with hot distilled water. The filtrate was evaporated almost to dryness, treated with dilute hydrochloric acid, and extracted with ether; the ether extract was dried with calcium chloride, the ether was driven off, and the residue was fractionated with a Widmer spiral column. This fractionation yielded 4 g of butyric acid:

B.p. 160-161°; d_4^{20} 0.9656; n_D^{20} 1.3985;

and 3.6 g of ethoxypropionic acid:

B.p. 108-110° at 10 mm; d_4^{20} 1.0515; n_D^{20} 1.4225; MR_D 28.54.

$C_5H_{10}O_3$. Calculated: MR_D 28.46.

Action of Butylmagnesium Bromide on 1-Ethoxy-5-chloropentene-3

An ether solution of butylmagnesium bromide was prepared from 6.2 g of magnesium chips and 35.9 g of butyl bromide. To this solution, chilled, 30 g of 1-ethoxy-5-chloropentene-3 was added drop by drop, and the reaction mass was heated over a water bath for 4 hours. When the reaction was over, the jellylike reaction mass was treated with cold water and dilute hydrochloric acid. The ether layer was separated and dried with calcium chloride, the ether was driven off, and the residue was distilled in vacuum with a Widmer spiral column. Yield: 3.6 g of the initial chloride, 18.7 g of 1-ethoxynonene-3:

B.p. 86-88° at 10 mm: d_4^{20} 0.8052; n_D^{20} 1.4280; MR_D 54.29.

$C_{11}H_{22}OF$. Calculated MR_D 54.17.

0.0889 g substance: 0.2534 g CO_2; 0.1024 g H_2O;
Found %: C 77.72; H 12.79;
$C_{11}H_{22}O$. Calculated %: C 77.64; H 12.94.

and 5.45 g of 1-ethoxy-6-β-ethoxyethyloctadiene-3,7:

B.p. 132-134° at 10 mm; d_4^{20} 0.8712; n_D^{20} 1.4470.

Action of Butylmagnesium Bromide on 1-Ethoxy-3-chloropentene-4

The reaction was carried out like that above. The ether solution of the Grignard reagent was prepared from 6.2 g of magnesium chips and 35.9 g of butyl bromide. Upon chilling, 30 g of 1-ethoxy-3-chloropentene-4 was added drop by drop, and the reaction mixture was heated for 3 hours. Fractionation yielded 3.4 g of the initial chloride, 18.3 g of 1-ethoxynonene-3:

B.p. 86-88° at 10 mm: d_4^{20} 0.8052; n_D^{20} 1.4270;

and 6.3 g of 1-ethoxy-6-β-ethoxyethyloctadiene-3,7:

B.p. 133-134° at 11 mm; d_4^{20} 0.8710; n_D^{20} 1.4460.

Action of Butylmagnesium Bromide on 1-Butoxy-5-chloropentene-3

The reaction was carried out like the preceding one. The ether solution of the Grignard reagent was prepared from 7.1 g of magnesium chips and 40.3 g of butyl bromide. To it there was added 40 g of 1-butoxy-5-chloropentene-3, and the reaction mass was heated for 4 hours. After the usual treatment of the latter and several fractionations with a Widmer spiral column we obtained 5.2 g of the initial chloride, 19.6 g of 1-butoxynonene-3:

B.p. 109-110° at 10 mm; d_4^{20} 0.8147; n_D^{20} 1.4340; MR_D 63.29.

$C_{13}H_{25}OF$. Calculated: MR_D 63.41.

0.0852 g substance: 0.2457 g CO_2; 0.1004 g H_2O.
Found %: C 78.64; H 13.09.
$C_{13}H_{25}O$. Calculated %: C 78.78; H 13.13.

and 7.4 g of 1-butoxy-6-β-butoxyethyloctadiene-3,7:

B.p. 171-173° at 11 mm; d_4^{20} 0.8623; n_D^{20} 1.4510; MR_D 87.23.

$C_{18}H_{34}O_2F_2$. Calculated MR_D 87.67.

0.0983 g substance: 0.2754 g CO_2; 0.1054 g H_2O.
Found %: C 76.40; H 11.9.
$C_{18}H_{34}O_2$. Calculated %: C 76.59; H 12.05.

Action of Butylmagnesium Bromide on 1-Butoxy-3-chloropentene-4

The reaction was carried out like the preceding one, with the same quantities of reagents. The reaction mass was heated for 5.5 hours.

Fractionation yielded 5.5 g of the initial chloride, 19.8 g of 1-butoxynonene-3:

B.p. 109-110° at 10 mm; d_4^{20} 0.8141; n_D^{20} 1.4335.

and 7.4 g of 1-butoxy-6-β-butoxyethyloctdiene-3,7:

B.p. 168-171° at 9 mm; d_4^{20} 0.8620; n_D^{20} 1.4500.

Action of Benzenemagnesium Bromide on 1-Butoxy-3-chloropentene-3

The ether solution of benzenemagnesium bromide was prepared from 7.5 g of magnesium chips and 49.8 g of benzenebromide. 40 g of the primary butoxychloropentene was added to the chilled solution of Grignard reagent. This reaction differed from those described previously in that the reaction of the benzene magnesium bromide with the chloride was accompanied with warming of the reaction mixture. After all the 1-butoxy-3-chloropentene-3 had been added, the reaction mixture was heated for six hours, but it was not observed to gel. Treatment and fractionation yielded the following reaction products: 2.7 g of benzene, 5 g of the initial chloride, and 32.6 g of 1-butoxy-3-phenylpentene-3:

B.p. 149-152° at 10 mm; d_4^{20} 0.9160; n_D^{20} 1.4940; MR_D 69.28.
$C_{15}H_{22}OF_4$. Calculated MR_D 69.04.

0.0933 g substance: 0.2821 g CO_2; 0.0843 g H_2O.
Found %: C 82.46; H 10.03.
$C_{15}H_{22}O$. Calculated %: C 82.56; H 10.09.

Action of Benzenemagnesium Bromide on 1-Butoxy-3-chloropentene-4.

The reaction was quite like the preceding one, with the same quantities of the chloride, benzene bromide, and magnesium used. Repeated fractionation of the reaction products yielded: 2 g of benzene, 5.8 g of the initial chloride, and 33.3 g of 1-butoxy-3-phenylpentene-3:

B.p. 148-151° at 10 mm; d_4^{20} 0.9156; n_D^{20} 1.4935.

Action of Magnesium on 1-Ethoxy-3-chloropentene-3

Into a flask fitted with a reflux condenser, a stirrer, and a dropping funnel there was placed 2.4 g of magnesium chips. The latter was activated by heating with crystalline iodine and then covered with absolute ether. Then some drops of ethyl bromide and an ether solution of 30 g of 1-ethoxy-3-chloropentene-3 were added. The reaction was continued with heating for 6 hours, with constant stirring. When the reaction was over, the reaction mass was diluted with water, and the ether layer separated and dried with calcium chloride.

Then the ether was driven off, and the residue fractionated in vacuum with a Widmer spiral column.

Repeated fractionation yielded: 9.3 g of the unreacted chloride and 0.1 g of 1-ethoxy-6β-ethoxyethyloctadiene-3,7:

B.p. 130-132° at 10 mm; d_4^{20} 0.8712; n_D^{20} 1.4470.

Action of Magnesium upon 1-Ethoxy-3-chloropentene-4

The reaction was similar to the foregoing one, with the same quantities of magnesium and the secondary chloride used, but the heating and stirring were continued for 3.5 hours.

After 3.3 g of the initial chloride had been distilled off, 14.2 g of 1-ethoxy-6-β-ethoxyethyloctadiene-3,7 was obtained:

B.p. 132-133° at 11 mm; d_4^{20} 0.8707; n_D^{20} 1.4460.

Action of Magnesium upon 1-Butoxy-3-chloropentene-3

A small amount of absolute ether, a few drops of ethyl bromide, and 30 g of 1-butoxy-3-chloropentene-3 were added to 2.05 g of activated magnesium chips. This reaction mass was then heated over a water bath with constant stirring. Heating was continued for 9 hours, after which the mixture was treated with water; the ether layer was removed and dried; the ether was driven off, and the residue fractionated in vacuum. 13.8 g of the initial chloride and 8 g of 1-butoxy-6-β-butoxyethyloctadiene-3,7 were distilled over:

B.p. 171-173° at 11 mm; d_4^{20} 0.8627; n_D^{20} 1.4510.

Reaction of 1-Butoxy-3-chloropentene-4 with Magnesium

The reaction was entirely similar to the preceding one, the same quantities of magnesium and the chloride being employed. Heating was continued for 6 hours. Fractionation yielded: 7.1 g of the initial chloride and 11 g of 1-butoxy-6-β-butoxyethyl-octadiene-3,7:

B.p. 171-173° at 11 mm; d_4^{20} 0.8623; n_D^{20} 1.4500.

Oxidation of 1-Ethoxy-6-β-ethoxyethyl-octadiene-3,7 by Potassium Permanganate

To a bottle containing 1100 ml of distilled water there were added 15 g of the hydrocarbon and, gradually with constant chilling, 67 g of potassium permanganate. After suitable treatment of the evaporated distillate with phosphoric acid, followed by extraction of the acids with ether, drying of the ether extract with calcium chloride, and fractionation, we obtained: a fraction boiling at 101-103°; ethoxypropionic acid with a b.p. of 108-110° at 10 mm, n_D^{20} 1.4210; and a fraction boiling at 200-222° at 10 mm as a thick yellow-brown liquid.

The presence of formic acid in the 101-103° fraction was proved by its reaction with ammoniacal silver nitrate. The solution turned black, and a deposit of metallic silver settled out.

SUMMARY

1. The reactions of isomeric ethoxy- and butoxychloropentenes with ethylmagnesium bromide, butylmagnesium bromide, and benzenemagnesium bromide were investigated.

2. It was found that these reactions are of the ionic type; the primary chlorides react normally, whereas the secondary ones react with complete allyl rearrangement.

3. The reactions of isomeric ethoxy and butoxychloropentenes with magnesium were studied. It was shown that in these reactions 1-ethoxy-6-β-ethoxyethyloctadiene-3,7 and 1-butoxy-6-β-butoxy-ethyloctadiene-3,7 are the principal reaction products.

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THE REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

II. REACTION OF ETHYL DIAZOACETATE WITH VINYL BUTYL ETHER IN THE PRESENCE OF COPPER

I. A. Dyakonov

A. A. Zhdanov Chemical Institute, Leningrad State University, awarded the Order of Lenin

In our preceding report [1] we pointed out that carrying out the Büchner-Loos reaction on the ethylenic components

$CH_2{=}CH{-}OC_4H_9$ and $CH_2{=}CH{-}OCO{-}CH_3$:

$$CH_2{=}CH{-}OC_4H_9 + CHN_2COOC_2H_5 \xrightarrow{Cu} CH_2{-}CH{-}OC_4H_9 + N_2\ldots \quad \text{II-a}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH{-}COOC_2H_5$$

$$CH_2{=}CH{-}OCOCH_3 + CHN_2COOC_2H_5 \xrightarrow{Cu} CH_2{-}CH{-}OCOCH_3 + N_2\ldots \quad \text{II-a}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH{-}COOC_2H_5$$

provides a new argument against accepting the mechanism of "pyrazoline condensation" for reactions that involve the liberation of nitrogen and belong to Class II. In that paper a number of other considerations were advanced against the prevalence of the hypothesis of intermediate formation – the cleavage of the pyrazoline derivatives in all the examples of such reactions described in the literature by various authors. On the other hand, the idea was emphasized that in many instances this hypothesis cannot be rejected because of the observed formation of pyrazoline derivatives and of their cleavage with the evolution of nitrogen and the opening of the cyclopropane ring.

It should be noted that the mechanism of reactions of aliphatic diazo compounds with ethylene bonds was considered in the preceding paper, and even earlier [2], in the light of the general problem of the activity of the ethylene bond when acted upon by electrophilic and nucleophilic reagents, whereas the question of using these reactions for the synthesis of new derivatives of the cyclopropane series has received almost no consideration in the author's research.*

The subsequent endeavors of the author of the present report were concentrated on the study of the following compounds:

$C_4H_9O{-}CH{-}CH{-}COOC_2H_5$ (I); $C_4H_9O{-}CH{-}CH{-}COOH$ (II); $CH_3COOCH{-}CH{-}COOC_2H_5$ (III)
$\qquad\qquad\quad CH_2 \qquad\qquad\qquad\quad CH_2 \qquad\qquad\qquad\quad CH_2$

---

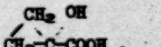
*Cf., however, "III. Reaction of Aliphatic Diazo Compounds with Allene Hydrocarbons" in this Journal [3].

which we were able to synthesize by reacting diazo acetic ester with vinyl butyl ether and, correspondingly, with vinyl acetate in the presence of copper powder.

The esters of alkoxy and acyloxy cyclopropanecarboxylic acids have hardly been described at all in the literature*; they are of undoubted interest research interest in connection with the feasibility of passing from them to 1-hydroxycyclopropane-2-carboxylic acid:

which has not been synthesized by anyone as yet.

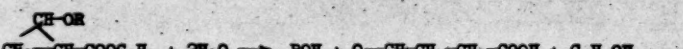
The isomeric 1-hydroxycyclopropane-1-carboxylic acid has been described by Ingold [3]:



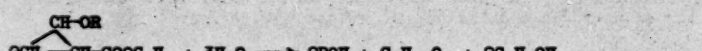
who synthesized this compound by means of a series of interesting transformations, starting with spirogindatoin.

Later, however, the quite thorough researches of Demyanov and Feofilaktov [4], who repeated Ingold's experiments, cast doubt on the cyclic structure of this acid.

Our endeavors to synthesize 1-hydroxycyclopropane-2-carboxylic acid by the hydrolysis of compounds (I), (II), and (III) met with no success. The hydrolysis itself could be easily effected both in acid (butoxy and acetoxy derivatives) and in alkaline (acetoxy derivatives) media, but in none of the experiments were we able to obtain 1-hydroxycyclopropane-2-carboxylic acid. Instead, either an aldehydic succinic acid was formed as the direct product of the isomerization of the cyclic acid, or a crystalline acid, $C_8H_{10}O_5$, was formed, its origin and structure having been the subject of investigation. The results of these investigations will be reported later.



or



where

$$R = C_4H_9 \text{ and } COCH_3.$$

The equations given above represent, in general, the hydrolysis of ethyl esters of 1-butoxycyclopropane-2-carboxylic acid and of 1-acetoxycyclopropane-2-carboxylic acid. The hydrolysis of 1-butoxycyclopropane-2-carboxylic acid falls under this same heading ($R = OC_4H_9$).

The instability of a hydroxy cyclopropanecarboxylic acid must, apparently, be due to the same causes as the instability of the simplest alcohol of the trimethylene series: cyclopropanol: in some unexplained fashion the strain in the

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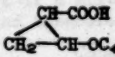
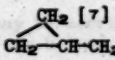
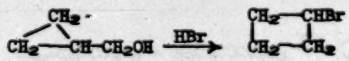
*Apart from the experiments of Rambaud [5] on the synthesis of ethoxycyclopropanecarboxylic acid and its ethyl ester.

three-membered ring imposes an 'interdiction' against the replacement of the ring hydrogen atom by a hydroxyl group. What is more, it might have been expected that a hydroxycyclopropanecarboxylic acid would have somewhat more stability than the unsubstituted cyclopropanol, owing to the stabilizing effect of the carboxyl group.

What involuntarily attracts attention in the hydrolysis reactions of compounds (I - III) is the ease with which the simple ether bonds in compounds (I - II) can be hydrolyzed by dilute mineral acids. Butoxycyclopropanecarboxylic acid (II) undergoes hydrolytic cleavage most easily: it is completely hydrolyzed at the O–C_4H_9 bond by heating with 0.5% sulfuric acid and largely so by heating with 20% acetic acid.*

This exceptional sensitivity to the action of hydrogen ions is characteristic of two different classes of compounds: the simple ethers of the trimethylene series, of which compounds (I) - (II) are derivatives, and the simple vinyl ethers. Both of them are easily cleaved under very mild conditions in the presence of hydrogen ions, forming an alcohol and an aldehyde (or an aldehydic acid, in the case of butoxycyclopropanecarboxylic acid) This analogy may be strengthened by the fact that the alcohols corresponding to the simple ethers of the trimethylene and ethylene series, in general, apparently cannot exist (cyclopropanol and vinyl alcohol), and that the cyclopropylcarbinols and allyl alcohols, which are fairly well known, exhibit a certain parallelism in their behavior:

Derivatives of the trimethylene series		Derivatives of the ethylene series	
[8]	Unknown; isomerizing to an allyl alcohol at the instant of its formation.	CH_2=CH–OH	Unknown, isomerizing to acetaldehyde at the instant of its formation.
		CH_2=CH–OC_4H_9	Rapidly hydrolyzed to C_4H_9OH and O=CH–CH_3 by dilute acids.
	Rapidly hydrolyzed to C_4H_9OH and O=CH–CH_2–CH_2–COOH by dilute acids.		
 [7]	When the hydroxyl is replaced by a halogen, the following re-arrangement takes place:	R–CH=CH–CH_2OH	When the hydroxyl is replaced by a halogen, an allyl rearrangement takes place.
			

This analogy also applies, as we know, to the chlorine derivatives of both hydrocarbons: with chlorine "at the double bond" and with a halogen atom at the trimethylene ring:

[8]	The halogen atom has extremely little mobility, not saponifying when heated with alkalies,	CH_2=CHCl	The halogen atom has extremely little mobility, not saponifying when heated with alkalies.

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*The ethyl ester of butoxycyclopropanecarboxylic acid is hydrolyzed with somewhat greater difficulty, but it, too, is completely hydrolyzed, however, when boiled with 10% sulfuric acid.

and we assume that in the future still other examples will be found to illustrate this resemblance between the compounds of the two series – up to a point.

The present paper describes a reaction between diazoacetic ester and vinyl butyl ether in the presence of copper, and the synthesis of the ethyl ester of 1-butoxycyclopropane-2-carboxylic acid. Conclusions are also reached regarding the structure of the principal and by products of this reaction from the data of the oxidation of these compounds.

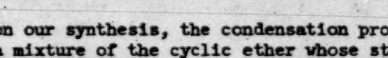
The reaction between diazoacetic ester and vinyl butyl ether is easy and smooth if a mixture of equal proportions of diazoacetic ester and vinyl ether is added drop by drop to a large excess of the vinyl ether heated to boiling, which contains an extremely fine suspension of copper powder (Natur Cupfer C). The reaction requires mechanical stirring and is accompanied by the evolution of nitrogen in quantities that approach those calculated from Equation (II-a).

The condensation product, the composition of which is $C_{10}H_{18}O_3$, is obtained by vacuum distillation of the liquid residue after the excess vinyl ether has been driven off. If the latter is also driven off in vacuum (100 mm, b.p. 39.5°), the yield of the condensation product is 80-83% of theory (Table 1, below). In this method of regenerating the solvent, the losses of the vinyl ether do not exceed 10% by weight of the excess ether.

Though our analytical data (molecular weight, composition formula, and molecular refraction) are in good agreement with the assumed structural formula (I):

$$C_4H_9O-CH\overset{CH_2}{\diagdown\diagup}CH-COOC_2H_5, \qquad (I)$$

based on our synthesis, the condensation product is not a single compound. It is a mixture of the cyclic ether whose structure has been indicated here, and unsaturated isomers of this ether, to which the following structure:

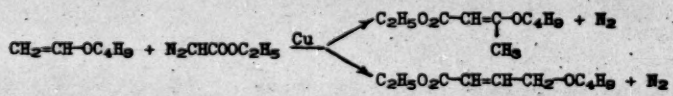


$$C_2H_5OOC-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-OC_4H_9 \quad \text{and} \quad C_2H_5OOC-CH=CH-CH_2-OC_4H_9$$

(IV) (V)

may be ascribed with more or less probability on the basis of oxidation data (see below).

These isomers are probably formed in accordance with Equation (II-b) [1]:



$$CH_2=CH-OC_4H_9 + N_2CHCOOC_2H_5 \xrightarrow{Cu} \begin{cases} C_2H_5O_2C-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-OC_4H_9 + N_2 \\ C_2H_5O_2C-CH=CH-CH_2-OC_4H_9 + N_2 \end{cases} \qquad (II\text{-}b)$$

since the cyclic ether itself is fairly stable and exhibits no tendency toward isomerization into open-chain ethers (as at heating to 150° and above).

Prolonged fractionation of the condensation product merely increases somewhat the boiling point range (103-109.5°), but does not make it possible to separate the isomers. No noticeable change in composition is observed during distillation, which is confirmed by the elementary analysis of all the fractions

recovered; but all the fractions prove to be "partially" unsaturated when tested with alkaline solutions of potassium permanganate.

Thus, we had to do without direct separation of the isomers, confining ourselves to isolation of the cyclic ether at the price of breaking down the the unsaturated isomers.

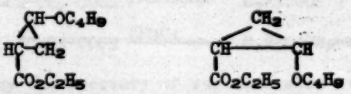
To do this we employed the method of oxidizing the condensation product by a cold permanganate solution, toward which trimethylene compounds are usually stable.

The consumption of permanganate also enabled us to make an approximate determination of the proportion of the unsaturated isomers in the condensation product. The computation, the results of which are given in Table 3, is based on the assumption of Formula (V) for the unsaturated compound. It must be concluded from these figures that the mean condensation product has the following composition: 98% of the cyclic ether, and 2% of the unsaturated isomers.

The yield of the cyclic ether is somewhat lower than that indicated above, owing to unavoidable losses during its isolation from the oxidation products; it amounts to 90% (average figure) of the weight used for the oxidation of the condensation product (Table 3).

In the oxidation products we found oxalic acid, as well as butyric and acetic acids. The presence of the latter two acids cannot be accounted for with sufficient accuracy since the separation of the mixture of silver salts of these acids was incomplete owing to the small quantities available (Table 4). Nevertheless, the data made us feel justified in reaching a conclusion concerning the structure of the unsaturated isomers, ascribing to them either Formula (IV) or Formula (V), as already stated.

The cyclic ether may exist in two stereoisomeric forms:



We were unable to provide experimental confirmation of this general stereochemical requirement.

As was to have been expected, the physical constants determined for the cyclic ether, as well as its molecular refraction, differ but little from the corresponding values found for the condensation product. In both cases the value of MR found exceeds that computed. For the cyclic ether this excess is 0.91, whereas the increment for the ring is 0.6-0.7 for most of the trimethylene compounds.

The slight exaltation of 0.2-0.3 for the ester of butoxycyclopropanecarboxylic acid may be due, in our opinion, to the peculiar "conjugation" of the carbethoxy group and the trimethylene ring: *

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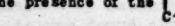
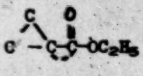
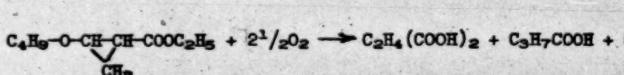
*Kizhner [9] found that the presence of the  complex causes an exaltation that equals approximately 1.
For the carboxylic acid $(CH_3)_2C\overset{CH_2}{\diagdown\!\!\diagup}CH\text{-}COOH$ he found the increment of molecular refraction to be 0.83; Rambaud [5] gives the increment as 1.00 for 1-ethoxycyclopropane-2-carboxylic acid.



We settled the question of the cyclic structure of the ether by means of the data on oxidation with potassium permanganate. The cyclic ether is quite stable in the presence of a cold solution of potassium permanganate, but when heated, especially when boiled with a permanganate solution, the ether is fairly quickly oxidized to succinic acid and a mixture of acetic and butyric acids, formed upon oxidization from the corresponding constituent radicals of the ether:



The formation of succinic acid was observed by Rambaud [5] in the oxidation of 1-ethoxycyclopropane-2-carboxylic acid (VI) and subsequently by us during the oxidation of 1-butoxycyclopropane-2-carboxylic acid (II) and of the ethyl ester of 1-acetoxycyclopropane-2-carboxylic acid (III):

(VI)

Apparently, the ability to be oxidized to succinic acid by permanganate is a general property of all the derivatives of cyclopropanecarboxylic acids that have an oxidized carbon atom ring in the β-position with respect to the carboxylic (or carbalkoxylic) group. The unsaturated isomers that correspond to any of the compounds listed above (I, II, III, and VI) should have yielded upon oxidation an acid with a smaller number of carbon atoms than succinic acid, such as:

This is why the recovery of succinic acid in the oxidation of the class of compounds here under investigation is an indication of their cyclic structure, and it must be supposed that the method suggested by us, involving the oxidation of trimethylenic compounds of this class will be the method to be employed in determining their structure.

We wish to express our indebtedness to Prof. M. F. Shostakovsky for the aid he rendered us during the performance of this research.

EXPERIMENTAL

I. Initial Preparations

We prepared the diazoacetic ester by the methods given in Gatterman-Willand [10] and Organic Synthesis [11]: from the hydrochloride of glycine. We found that when 100 g or more of glycine is used, $2N\ H_2SO_4$ must be used, and not a 4N acid as recommended by Gatterman-Willand, because the reaction is exothermic. Moreover, it was found advisable to neutralize the solution of glycine hydrochloride with dry soda before the reaction is begun. The yield of

crude ethyl diazoacetate was 85% of the theoretical, whereas the yield of the preparation purified by steam distillation in vacuum (b.p. 45.5-46.5° at 13 mm) was 67-70% of theory.

Substituting the crude preparation for the ethyldiazoacetate refined by distillation had but little effect upon the yield of the end product of our reaction; that is why we preferred to use the crude preparation, especially since refining entailed the loss of considerable time as well as a lower yield of the diazoacetic ester. The glycine hydrochloride was prepared by a minor modification of a method proposed by Harries and Weiss [12]. Yield: 90-94% of the theory, b.p. 144°.

Vinyl butyl ether. The crude product was washed free of butyl alcohol with water, dried over fused potash, and fractionated with a column. B.p. 93-94°.

II. Condensation of Vinyl Butyl Ether With Diazoacetic Ester in the Presence of Copper

Method of Preparation. 300 ml of vinyl butyl ether, in which 1 g of copper powder* is kept in lively movement by means of rapid stirring, is heated to gentle boiling. Then, while the reaction mass is constantly stirred, a mixture of 40 g of the diazoacetic ester and 100 ml of the vinyl butyl ether is added drop by drop.** If the apparatus is gastight, the nitrogen evolved can be collected in a gasometer. By the end of the reaction nearly the theoretical quantity of nitrogen is collected. The reaction mixture is kept at the boiling point throughout the experiment. The reaction rate may be easily gauged by the liberation of nitrogen; it can be easily regulated by varying the rate of addition of the diazo component. Thus, control of the reaction is entirely in the hands of the experimenter. After all the diazo component has been added, the reaction mixture is kept boiling for another 20 to 30 minutes, after which it is cooled to room temperature, and the copper filtered out (without suction).

The filtrate is distilled in a 100-mm vacuum to remove the excess vinyl ether. If the receiver is chilled with snow, the yield of the regenerated vinyl ether will be 330 (90% of theory). The b.p. of vinyl butyl ether at 103 mm is 39.5°. The diazoacetic ester is not recovered, since it is totally disintegrated by the copper powder in the course of the reaction.

After the solvent had been driven off, the crude product weighed 64 g and gave the following results upon fractionation:

1st fraction: b.p. 105-107° at 14 mm; yield 52.5 g;

2nd fraction: b.p. 107-108.5° at 14 mm; yield 2.5 g;

The undistilled residue was resinous; it weighed about 5 g. Both fractions are nearly the pure ether $C_{10}H_{18}O_3$. The yield of the condensation product was 55 g (84.3% of theory).

In Table 1 we have combined the results of the experiments on the condensation of ethyl diazoacetate with vinyl butyl ether in the presence of copper. The lower yields in the first two runs is due to the fact that the recovery of the excess vinyl ether was not done in vacuo but at ordinary pressure. This causes heavier tarring of the reaction product, and the undistilled residue

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*Natur Cupfer C

**In most cases we used a mixture consisting of approximately equal volumes of both reaction ingredients (Table1).

after fractionation of the condensation product weighs more.

The boiling temperature ranges grow wider when the reaction product is fractionated in a column (Runs 5 and 6). However, the composition formulas of all the isolated fractions correspond more or less to $C_{10}H_{18}O_3$, the formula for an ether of cyclic structure. The wide intervals for the boiling point are due apparently to spatial and structural isomerism.

Table 1

Experiments on the Condensation of Ethyl Diazoacetate with Vinyl Butyl Ether in the Presence of Copper

Test No.	Charge of ethyl diazo-acetate g	Charge of vinyl butyl ether, ml		Recovered vinyl ether		Yield of Reaction product %	Boiling point of reaction product
		In drop-ping funnel	In re-action flask	ml	% of theor-etical yield		
1	19	10	140	–	–	51	106-108, 14 mm
2	57	300	100	–	–	65.6	94.5-97.5, 8 mm
3	38	100	300	330	89.9	81.3	95-97, 8 mm
4	40	100	300	330	90.4	84.3	105-108.5, 14 mm
5	80	100	400	415	95.4	82.6	105-109, 14 mm
6	142.5	155	400	390	90.7	80.4	92-97, 7 mm
7	57	50	325	310	95.4	80.3	103.5-106, 14 mm
8	103.5	100	400	380	90.8		
9	67	65	360	350	95.6	78.1	103-105, 12 mm
10	67	75	350	350	95.6	75.2	103-105, 12 mm

In runs 7 and 8, the reaction products of both runs were combined after the vinyl ether had been driven off and fractionated together.

The yield of the reaction product was computed on the basis of the aggregate charge of ethyl diazoacetate in the two runs.

The last four runs were made with crude, undistilled ethyl diazoacetate.

Analytical data on the condensation product. The reaction products of Runs 2 and 4 were combined, and their aggregate 115 g was subjected to vacuum distillation with a D.V.Tishchenko column. No sharp changes in the boiling point were observed. The distillate was artificially divided into the following 5 fractions for analytical purposes.

Table 2

Distillation of Fractions of the Condensation Product

Fraction No.	1	2	3	4	5	Undistilled residue
Wt. of fract.	3 g	14 g	61 g	14 g	13g	8 g
B.p, 14 mm.	up to 103	103-104.5	104.5-105.5	105.5-106.5	106.5-109.5	–

Analysis of Fraction 2

0.1463 g substance: 0.3468 g CO_2; 0.1334 g H_2O.
Found %: C 64.65 H 10.21.
$C_{10}H_{18}O_3$. Calculated %: C 64.49 H 9.74.

Analysis of Fractions 3 and 4

0.0984 g substance: 0.2322 g CO_2: 0.0870 g H_2O.
Found %: C 64.37; H 9.89.
$C_{10}H_{18}O_3$. Calculated %: C 64.49; H 9.74.

Analysis of Fraction 5

0.0935 g substance: 0.2197 g CO_2; 0.0882 g H_2O.
Found %: C 64.08; H 10.54.
$C_{10}H_{18}O_2$. Calculated %: C 64.49; H 9.74.

Only the composition of the last fraction, which constitutes only 12% by weight, differs somewhat from the computed formula. The composition of the other fractions agrees with the theoretical requirements.

Determination of Molecular Weight for a Mixture of Fractions 2 and 3

0.1722 g substance: 16.38 g C_6H_6: Δt 0.290°.
0.3606 g substance: 16.38 g C_6H_6: Δt 0.630°
Found %: M 181.2, 177.4
$C_{10}H_{18}O_3$. Calculated : M 186.1.

Physical Constants and Molecular Refraction of a Mixture of Fractions 2 and 3

B.p. 104.5-105.5° at 14 mm; d_4^0 0.9759; d_4^{18} 0.9594; n_α^B 1.431.

Found: MR_α 50.17.

$C_{10}H_{18}O_3$. Calculated: MR_α 49.26; increment 0.91.

The observed change with temperature of the values of specific gravity and refractive index of various samples of our ether is as follows:

Specific gravity		Refractive index	
d_4^0	0.9759		–
d_4^5	0.9731	n_α^5	1.437
$d_4^{6.5}$	0.9725	n_α^7	1.436
d_4^8	0.9721	$n_\alpha^{8.5}$	1.435
d_4^{11}	0.9681	n_α^{11}	1.434.

III. Synthesis of the Ethyl Ester of Butoxycyclopropanecarboxylic Acid and Determination of its Structure

A 2% solution of permanganate was added in small batches with constant stirring to 150 g of the condensation product until the purplish color of the reaction mixture dissappeared upon standing. The addition of permanganate in

the cold ceased after the 14 g of the reagent had been added. The solution, which was allowed to stand overnight, had lost its purplish color by morning. The permanganate that had not entered into the reaction was eliminated with 50 ml of a 4% solution of sodium sulfate. The actual quantity of permanganate used to oxidize the ester was 12.3 g. The deposit of manganese dioxide that settled out during oxidation was filtered out with suction, then removed from the filter and washed, first with sulfuric ether to extract the unoxidized product, and then with hot water to leach out the adsorbed salts of the organic acids.

The main filtrate consisted of two layers: the lower one aqueous, and the upper one, oily, the trimethylene ester. After removal of the aqueous layer the crude trimethylene ester weighed 143 grams. The aqueous layer was extracted with sulfuric ether, and the ether extracts, together with the ether extract of the manganese dioxide, were combined with the trimethylene ester. The reaction product was dried with calcium chloride and, after the solvent had been driven off, fractionated in vacuum with a D. Tishchenko column.

Fraction I: 93-95°, 8 mm, 132.7 g; Fraction II: 95-98°, 8 mm, 8.2 g.

Both fractions are unaffected by a permanganate solution in the cold. The yield of the condensation product was 140.9 g based on the total of Fractions I and II (94% of theory, based on the product taken for the oxidation reaction).

The results of the various runs for synthesizing the trimethylene ester are listed in Table 3.

Table 3

Experiments in Oxidizing the Condensation Product

Test No.	Initial Reagents: Condensation product, g	Initial Reagents: $KMnO_4$, g	Unsaturated isomers determined by consumption of $KMnO_4$: g	Unsaturated isomers determined by consumption of $KMnO_4$: % by wt. of condensation product	Output of trimethylene ester: g	Output of trimethylene ester: % by wt. of condensation product	Output of trimethylene ester: % theory based on diazoacetic ester	Boiling pt. of trimethylene ester
1	10	–	–	–	8.2	82	–	90.5-93, 7 mm
2	39	–	–	–	33.5	86	–	92.5-95.5, 8mm
3	102	8.4	1.88	1.84	89	88	–	108-111, 16mm
4	150	12.3	2.71	1.81	141	94	–	93-98, 8 mm
5	209	14.5	3.20	1.53	185.8	88.9	71.4	102-103, 12mm
6	168	16.7	3.68	2.19	150	89.4	69.7	110-111, 17mm
7	120	33	7.21	6.00	107	89	69.7	90-96.7, 8mm

It follows from the data of Table 3 that the yields of the trimethylene ester range from 86-94% of theory (if Test 1 is excluded), based on the condensation product used for oxidation (Col. 7). Only for the three last tests did we possess enough data to compute the output of the ester in terms of the initial diazoacetic ester. The yield averages 70% of theory (Col. 8). Col. 3 gives the amount of permanganate (in grams) used in oxidizing the unsaturated isomers contained in the initial product alongside the cyclic isomer. The

amounts of unsaturated isomers, cited in Cols. 4 and 5 (in grams) and in percentages by weight of the initial product, were computed in terms of the permanganate used to oxidize the unsaturated isomers, on the assumption that the most appropriate way of representing them is by means of Formula (V). This formula requires 8 gram equivalents of oxygen for the complete oxidation of 1 mole of the isomer to oxalic, butyric, and acetic acids. If, on the other hand, Formula (IV) is correct, the same oxidation end products would require 7 gram equivalents of oxygen per mole of the unsaturated ether. Thus, the permanganate consumption will be about the same in both cases, the slight difference not affecting the computation result appreciably.

Investigation of the Oxidation Products in Aqueous Solution

The aqueous solution of the salts after oxidation, combined with the wash waters of the manganese peroxide, were concentrated down to a volume of 150 ml, acidulated with a small amount of sulfuric acid, and subjected to steam distillation. When the steam-volatile acids were distilled, they passed over to the receiver, the nonvolatile acids remaining behind in the distilling flask.

It was assumed that the distillate contained butyric and acetic acids, and that oxalic acid was present in the solution left behind in the distilling flask. We actually isolated oxalic acid from the solution as its Ca salt after the ions of sulfuric acid had been removed from the solution.

0.1263 g substance: 0.0492 g CaO.
0.2129 g substance: 0.0820 g CaO.
Found %: Ca 27.85, 27.54.
$CaC_2O_4 + H_2O$. Calculated %: Ca 27.30.

The distillate yielded silver salts of the acids that were steam-distilled. The salts, however, proved to be useless for analysis owing to their rapid decomposition, even in solution. Prolonged heating of a solution of these salts over a water bath enabled us to get rid of the traces of unstable salts and to obtain some silver-salt fractions from the filtrate (after the deposited silver had been filtered out) that were stable enough for us to make our determinations. Analysis of the various fractions indicated that this is a mixture of salts of two acids, but in none of the tests we made were we able to accumulate enough of the salts to separate them completely. However, in some instances we were able to obtain results (see Table 4) that are close to those computed for the salts of butyric and acetic acids (Test 1, 1st fraction and Test 3, 4th fraction).

Table 4

Analysis of the Fractions of Silver Salts of the Acids Obtained in Various Experiments to Oxidize the Condensation Product

Test No.	Silver-salt fractions	Weight of silver salt, g	Weight of silver after calcining, g	Percent of silver
1	1st fraction	0.0785	0.0440	56.06
	2nd fraction	0.0660	0.0396	60.00
2	1st fraction	0.1300	0.0740	56.92
		0.1970	0.1127	57.19
	2nd fraction	0.1255	0.0766	61.17

Table 4, contd.

Test. No.	Silver-salt fractions	Weight of silver salt, g.	Wt. of silver after calcining	Percent silver
3	1st fraction	0.1158	0.0703	60.7
	2nd fraction	0.1456	0.0902	61.95
	3rd fraction	0.1001	0.0625	62.5
	4th fraction	0.1663	0.1054	63.5

$C_4H_7O_2Ag$. Calculated %: Ag 55.39.
$C_2H_3O_2Ag$. Calculated %: Ag 64.57.

Analytical Data for Ethyl Ester of Butoxycyclopropanecarboxylic Acid and Determination of its Structure by Oxidation

B.p. 90.5-93° at 7 mm; 102-103° at 11-12 mm; 110-111° at 17 mm; d_4^0 0.9750; d_4^{20} 0.9677; d_4^{20} 0.9563; n_α^{20} 1.435.

Found: MR_α 50.17.
$C_{10}H_{18}O_3$. Calculated: MR_α 49.26.
0.1198 g substance: 0.2822 g CO_2; 1.1090 g H_2O.
0.1439 g substance: 0.3407 g CO_2; 0.1262 g H_2O.
Found %: C 64.22, 64.58; H 10.17, 9.81.
$C_{10}H_{18}O_3$. Calculated %: C 64.49; H 9.75.

Oxidation of the Ester by Potassium Permanganate

5.6 g of the trimethylene ester (0.03 mole) was heated to gentle boiling while 300 ml of a 3% solution of potassium permanganate (10 g $KMnO_4$ in 300 ml of water) was rapidly stirred in. When the purplish color had disappeared, new batches of potassium permanganate were added, this time in dry form. A total of 9 g of powdered potassium permanganate was added. After the solution had been decolorized, the reaction mixture was cooled to room temperature, and the manganese dioxide filtered out. The manganese dioxide was washed with water, and the filtrate, together with the wash waters, concentrated over a water bath to an aggregate volume of 60 ml.

This solution, acidulated with the requisite quantity of sulfuric acid, was extracted with ether in a perforater. The extract was a mixture of solid and liquid acids. The solid acid was filtered out of the liquid acids, washed with ether, and crystallized from hot water. B.p. 184°. Yield 0.82 g (after crystallization).

Determination of the neutralization equivalent yielded a figure close to that computed for succinic acid:

0.1777 g substance: 36.9 ml 0.1N NaOH.
0.1751 g substance: 36.4 ml 0.1N NaOH.
Found equiv.: 59.80 59.80.
$(CH_2)_2(COOH)_2$. Calculated equiv.: 59.03.

A mixed sample with the latter caused no depression.

The liquid acids were distilled at ordinary pressure. Distillation

yielded 1.7 g of a distillate with a b.p. of 100-105°. The distillate was diluted with a large quantity of water and heated with silver carbonate for several hours until its reaction was neutral. The excess silver carbonate was filtered out of the hot solution, which was then concentrated in vacuum over a water bath at 40°. The silver salts of the acids, which separated out as the solution grew more concentrated, were filtered out and analyzed. Fractional evaporation in vacuum yielded 5 fractions of the silver salts, but only 4 of them could be analyzed for their silver content.

Fraction II: 0.1760 g substance: 0.1021 g Ag; Found %: Ag 58.0
Fraction III: 0.1774 g substance: 0.1068 g Ag; Found %: Ag 60.2
Fraction IV: 0.1601 g substance: 0.1005 g Ag; Found %: Ag 62.7
Fraction V: 0.1449 g substance: 0.0917 g Ag; Found %: Ag 63.7.
$C_4H_7O_2Ag$. Calculated %: Ag 55.4
$C_2H_3O_2Ag$. Calculated %: Ag 64.6.

Although we were unable to effect complete separation of the fractions into salts of butyric and acetic acids, when we bear in mind the variation in the silver content in these fractions, it must be assumed that the latter actually are mixtures of the acids expected to be present here. Fraction I, which was not analyzed, should have exhibited an even lower percentage of silver, closer to that calculated for silver butyrate.

SUMMARY

1. It has been shown that diazoacetic ester reacts with vinyl butyl ether in the presence of copper and at the boiling point of the ether, liberating nitrogen and forming a reaction product, the composition of which is $C_{10}H_{18}O_3$ (yield 80% of theory).

2. It has been shown, on the basis of the data on the oxidation of the reaction product by a cold solution of potassium permanganate, that about 98% of the reaction product consists of the ethyl ester of 1-butoxycyclopropane--2-carboxylic acid, only 2% by weight representing unsaturated isomers of this ester.

3. Though oxalic acid, as well as a mixture of butyric and acetic acids, was obtained as a result of the oxidation of the unsaturated isomers, only preliminary statements can be made concerning the structure of these isomers owing to the wide choice of isomers that may be made in this case.

4. The ethyl ester of 1-butoxycyclopropane-2-carboxylic acid was isolated from the reaction product with a yield that was 70% of theory, based on the initial diazoacetic ester used in the synthesis.

5. The ethyl ester of 1-butoxycyclopropane-2-carboxylic acid is saturated with respect to a cold solution of permanganate, but is oxidized by the latter when heated, forming succinic, butyric, and acetic acids, corresponding to the cyclic structure of the ester.

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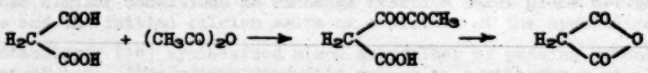
RESEARCH IN β-LACTONES AND β-LACTONIC ACIDS

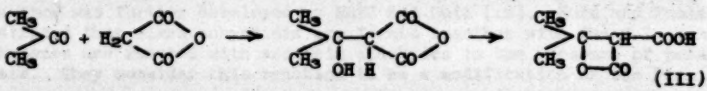
V. MIXED ANHYDRIDES OF MALONIC AND ACETIC ACIDS

N. S. Wulfson

In 1913, Ott [2] in his study of the reaction between acetic and malonic acids in acetic anhydride in the presence of concentrated sulfuric acid, first described by Meldrum [1] in 1908, assumed that the first stage of the reaction is the formation of a mixed anhydride of malonic and acetic acids (I). In Ott's opinion, this mixed anhydride is disproportionated into symmetrical malonic anhydride (II) in the process of condensation with acetone (like the action of acetic anhydride on diethylmalonic acid [3]) resulting in the formation of β-lactonic acid (III):



(I) (II)



(III)

Michael and Ress [4], examining this reaction, reject the mechanism proposed by Ott, considering that the mixed anhydride (I) participates in the reaction directly. Neither Ott nor Michael and Ress furnish any experimental corroboration for the correctness of the reaction mechanism suggested nor is there any proof of even the existence of the mixed anhydrides.

The supposition that the first stage of the reaction is the formation of a mixed malonic-acetic anhydride, which reacting with acetone leads to the formation of β-lactonic acid, seemed to me to be quite plausible. Much less likely seemed to be Ott's assumption that this mixed anhydride is disproportionated into a simple anhydride before condensing with the acetone.

Continuing my study of the β-lactonic acids, I felt it necessary to clear up this very important problem. It is all the more important in that the question of the existence of mixed anhydrides had not been conclusively settled up to very recently.

Mixed anhydrides were first synthesized by Gerchardt in 1853 [5], at the same time as the discovery of the symmetrical anhydrides, by reacting halogen acid anhydrides with the sodium salts of other acids. The reaction discovered by Gerchardt was confirmed by a number of other authors (Loir [6], Tassinari [7],

and Anthoine [8]). In 1887 Authenrith [9,10] found that mixed anhydrides together with symmetrical anhydrides are formed when acetic anhydride is boiled with monobasic acids. Behal [11] synthesized acetic-formic anhydride by this method.

In 1895 Roussat [12] concluded from the data of the fractional distillation of mixed anhydrides at standard pressure and in vacuum that they do not exist at all, but are a mixture of simple anhydrides. Detailed examination of the data cited by Roussat, however, permits the conclusion that disporportionation sets in only during distillation and not very rapidly, since the fractions corresponding to the simple anhydrides are accumulated only gradually, after repeated distillation.

Behal [13], comparing the chemical behavior of a mixed anhydride with that of an equimolecular mixture of simple anhydrides, confirmed the existence of the former. Authenrith [14] likewise rejected Roussat's assertion. Finally, the existence in principle of mixed anhydrides is supported by comparison of their hydration rate with that of a mixture of symmetrical anhydrides [15,16].

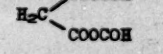
The synthesis of mixed ketones in the pyrolysis of calcium salts of various organic acids is circumstantial evidence of the existence of mixed anhydrides even at high temperatures. E. M. Bamdas [27] demonstrated that the respective anhydride is obtained as an intermediate product during the pyrolysis of copper and silver salts of opianic, benzoic, and acetic acids. Dosis and Leucaditis [17] believe that in the reaction to synthesize mixed ketones mentioned above, mixed anhydrides are formed first. This is borne out by the fact that under similar conditions no exchange reaction takes place between the radicals and the initial calcium salts or a mixture of the symmetrical ketones.

Staudinger [18] synthesized mixed anhydrides by passing ketones through solutions of acid. The author used this method to synthesize a mixed anhydride of diphenylacetic and benzoic acids in crystalline form, which permits us to consider the question of their existence as definitely settled. Staudinger's method was further developed by Hurd and Dull [19]. Hurd and Thomas [20] demonstrated that mixed anhydrides are formed together with the β-lactones when ketenes are reacted with aromatic aldehydes in the presence of potassium acetate. They consider this reaction to be a modification of the Perkin reaction.

All that has been said up to now refers solely to monobasic acids. In the light of the research I am doing the question of the mixed anhydrides of dibasic and monobasic acids and, particularly, of malonic acid, was of especial interest. Gerchardt and Chiozza [21] had already endeavored to synthesize mixed anhydrides of di- and monobasic acids, but all they found was the formation of a mixture of symmetrical anhydrides. The ease with which such mixed anhydrides are disproportionated is also noted by Oddo and Mannuelli [22].

The first mixed anhydride of this type was synthesized by Henle [23] in 1906. When boiling β,γ-diphenyladipic acid with acetyl chloride, he obtained a mixed diphenyladipoacetic anhydride instead of the expected symmetrical anhydride.

Diels and Lalin [24] synthesized a mixed anhydride of malonic and formic acids (IV) as white crystals, m.p. 78°, by letting carbon suboxide act upon formic acid in a solution of liquid SO_2.



(IV)

With acetic acid the authors obtained a sirupy product, very unstable, probably of the same structure. Staudinger and Bereza [25] confirm the existence of

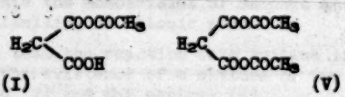
these anhydrides.

All the mixed anhydrides easily break down into the respective acids when acted on by water. When acted on by alcohols and aniline, Behal [11] noted that ethers and acid anilides, less rich in carbon, are the principal products. Authenrith [4] in fact, asserts that a mixture of ethers of both acids is obtained. Staudinger also obtained a mixture of two anilides [18].

It seems to me that no generalization can be made in this matter and that this question must be considered separately in each individual case.

Even Meldrum [1] noted that when a few drops of concentrated sulfuric acid were added to a mixture of malonic acid and acetic anhydride rapid solution takes place accompanied by a sharp drop in temperature, which points to the presence of a chemical reaction. Ott [2], driving off the excess acetic anhydride and the acetic acid formed from the solution thus obtained, found a thick, sirupy mass, which he treated as a "mixed anhydride" and used for further condensation with acetone without first separating the sulfuric acid (we shall refer to this preparation henceforth as "Ott's reagent").

When methanol is added to Ott's reagent (Experiment 1), a violent reaction sets in, resulting in a mixture of methyl acetate with mono- and dimethyl malonates. Since the formation of malonic esters might be the result of the catalytic action of the sulfuric acid in the Ott's reagent, the reagent was first extracted with absolute ether, and the absence of sulfuric acid checked by the barium-chloride reaction (Experiment 2). In this instance, the reaction with methanol is just as intensive, and a mixture of the same products is formed. Moreover, it was found that under similar conditions malonic acid is not esterified by methanol with a small amount of sulfuric acid if no acetic anhydride is present. Thus, though the formation of methyl acetate may be attributed to the addition of some amount of acetic anhydride to Ott's reagent, the formation of the malonic esters can be due solely to the presence in this reagent of a mixed anhydride of malonic and acetic acids, and, possibly, of a mixture of two such anhydrides; and acid (I) and a neutral (V) one:



(I) (V)

To check this supposition, I endeavored to prepare the mixed anhydrides of malonic and acetic acids by letting acetyl chloride act upon the acid and neutral silver salt of malonic acid, in suspension in absolute ether (Experiments 5 and 6). After the precipitate of silver chloride had been removed, methanol was added to the filtrate, and the resulting reaction yielded the mono- and dimethyl malonates, respectively. These tests, on the one hand, prove that Ott's reagent contains a mixture of two anhydrides, and on the other, they demonstrated that these anhydrides can be obtained by means of the classical reaction for the formation of mixed anhydrides [5].

It is known [28] that a solution of malonic acid in acetic anhydride gradually turns brown with green fluorescence, this being especially strong in the presence of acetic acid. It was not unlikely, it seemed to me, that mixed anhydrides are formed slowly when malonic acid is dissolved in cold acetic anhydride, but more rapidly when the latter is heated somewhat. Gradually throughout the course of 24 hours, a sirupy brown mass was obtained when malonic acid was dissolved in a large excess of acetic anhydride (at room temperature). It reacts with methanol as intensively as does Ott's reagent, forming a mixture of

the same products (Experiment 3). The reaction of methanol with the preparation produced by 4 hours of heating malonic acid with an excess of acetic anhydride to 60-70° yielded the same result (Experiment 4). Hence, malonic acid reacts directly with acetic anhydride (for the sake of brevity, we shall henceforth call this preparation "primary mixed anhydride"), the sulfuric acid serving merely as a catalyst — in the preparation of Ott's reagent.

We ran a series of tests (Experiments 7 - 11) to check whether the reaction with alcohols is a general reaction. The primary alcohols used were n-butyl and lauryl alcohols; the secondary alcohol was octanol-2; the tertiary was trimethylcarbinol; and the last one was phenol. In every case, the reaction with the primary mixed anhydride yielded a mixture of the corresponding mono- and dimethyl malonates and the acetate. Isolation in pure form proved to be impossible for most of the monomalonates because of their instability upon heating. We were able to vacuum distill only the monomethyl malonate with slight decomposition (b.p. 145-148° at 50 mm). The only data we can use in judging them are those of titration and of the analysis of the silver salt (the distilled monomethyl malonate was subjected to elementary analysis). The monolaurynyl and monophenyl malonates proved to be crystalline substances (m.p. 42-43° and 65-68°, respectively), and therefore could be purified by crystallization and then subjected to elementary analysis.

It was thus established that the reaction with mixed anhydrides synthesized as the result of treating malonic acid with acetic anhydride is a universal reaction of all alcohols.

Another reaction that can serve as indirect proof of the existence of a mixed anhydride is the reaction with aniline.

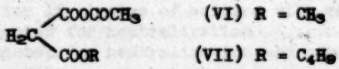
When aniline is added to the primary mixed anhydride, an extremely violent reaction ensues, but the only product one is able to isolate is the dianilide of malonic acid. When the reaction is effected under milder conditions in a solution of absolute ether, which does not allow the temperature to rise so high, we are able to isolate the monoanilide of malonic acid and some acetanilide, in addition to the dianilide of malonic acid.

It is thus evident that the reaction with aniline is like that with the alcohols, which confirms the existence of a mixture of two anhydrides of malonic and acetic acids: the acid (I) and the neutral (V).

All our endeavors to isolate these mixed anhydrides in pure state from Ott's reagent, the primary mixed anhydride, or the products of the reaction of acetyl chloride with the acid or neutral silver salt of malonic acid proved fruitless. Neither freezing, selection of solvents, nor vacuum distillation yielded the desired result. This agrees with Behal's observation [11] that the product obtained as a result of the action of carbon suboxide upon acetic acid loses acetic anhydride upon standing for a long time in vacuum (0.1-0.2 mm) at room temperature. Despite this failure, it seemed advisable not to limit ourselves to an indirect proof of the existence of mixed malonic-acetic anhydrides, but to show, by some example or other, that they are actually real. Bearing in mind the statements in the literature that mixed anhydrides of monobasic acids are more stable than those of dibasic acids, as well as the requirement of not departing from the derivatives of malonic acid, I used the acid malonates.

When a few drops of concentrated sulfuric acid are added to a mixture of monomethyl malonate and acetic anhydride, considerable heat is evolved, indicating the presence of a chemical reaction (Experiment 14). We obtain a colorless oily substance, which distills at 70-71° at 7 mm without decomposition, n_D^{26} 1.4106.

The odor of acetic acid appears after the substance is left standing for a long time exposed to the air. The substance reacts with methanol to form dimethyl malonate. With aniline it yields acetanilide and monomethyl malonate. Boiling this substance in a 65% alcohol solution with an alkali and p-nitrobenzyl bromide yields a mixture of the p-nitrobenzyl esters of malonic and acetic acids, which are separated by fractional crystallization. These esters are identified by their melting points and by mixed samples with analytical standard substances. All the chemical properties mentioned, together with the analytical data justify the assertion that the product obtained by the action of monomethyl malonate with acetic anhydride in the presence of concentrated sulfuric acid is the mixed anhydride (VI):



(VI) R = CH_3

(VII) R = C_4H_9

(VIII) R = C_6H_5

By analogy with the fact that Ott's reagent yields the β-lactone of isopropylidenemalonic acid when reacted with acetone [1,2], it might have been expected that the mixed anhydride (VI) would yield the methyl ester of the β-lactone of isopropylidenemalonic acid when treated with acetone. No reaction takes place, however.

As in the preparation of Ott's reagent, sulfuric acid is a catalyst in the reaction described above. This is proved by the fact that mono-n-butyl malonate, when treated with acetic anhydride, yielded the mixed anhydride (VII), which is analogous to (VI), with no sulfuric acid present (Experiment 15). The properties of this compound are similar to those described for the methyl derivative. A mixed anhydride was synthesized from monophenyl malonate by the same procedure (Experiment 16); it was found to be a crystalline substance with a m.p. of 55.5-56° possessing the same properties (VIII).

All the data cited above enable us to consider it proved that both the mixed malonic-acetic and the mixed monoalkyl (or monoaryl) malonic-acetic anhydrides exist.

In conclusion I wish to express my profound gratitude to Academician V.M.Rodionov and Prof. M.M.Shemyakin, whose advice and counsel have contributed considerably to the success of this research.

EXPERIMENTAL

Synthesis of Mono- and Dimethyl Malonates

1. To 10 g of finely powdered malonic acid and 40 g of acetic anhydride there is added 3 drops of concentrated sulfuric acid, and the whole is agitated until complete dissolution is obtained, which is accompanied by strong chilling. The solution is left to stand overnight, and then all the excess of acetic anhydride is driven off in vacuum (3-5 mm) at a bath temperature of 40-50°. The light-yellow, sirupy residue is allowed to cool, after which 15 ml of absolute alcohol is added drop by drop; this is accompanied by the evolution of considerable heat. After the mixture cools, it is poured into water and extracted with ether, and the ether solution treated with soda. The ether solution is washed with water and dried, the ether driven off, and the residue distilled. The product is 1.5 g of a 54-59° fraction; n_D^{20} 1.3590 (methyl acetate boils at 57°; n_D^{20} 1.35935). The residue is distilled in vacuum. Yield: 7.6 g (60% of

theory) of dimethyl malonate with a b.p. of 74-77° at 13 mm, n_D^{20} 1.4140 (dimethyl malonate has a b.p. of 78° at 14 mm, n_D^{20} 1.41398). The soda solution is neutralized with 25% sulfuric acid, extracted with ether, washed with water, dried, and decolorized with activated charcoal, and the ether driven off. The residue is a light-yellow, mobile liquid, which distills in vacuum with slight decomposition at 145-148° (50 mm). The yield of monomethyl malonate is 3.8 g (24.7% of theory).

Titration

0.1518 g of the substance: 10 ml of 70% alcohol.

0.1N NaOH consumed in the cold, against phenolphthalein.....	13.3 ml
Consumed after 15 minutes of boiling with excess alkali.....	26.94 ml
$C_4H_6O_4$. Computed for neutralization	13.4 ml
Computed for neutralization and saponification	26.8 ml

Analysis of Silver Salt

Found %: Ag 48.2

$C_4H_5O_4Ag$. Calculated %: Ag 48.0.

2. Ott's reagent is prepared from 10 g of malonic acid as described above. After the acetic anhydride is removed, the sirupy mass is extracted with absolute ether. The small quantity of crystals (0.3 g) that settles out is separated, and a barium-chloride test is used to prove that there is no sulfuric acid in the ether solution. Then 15 ml of absolute methanol is added to the solution. Further treatment is the same as in Exp. 1. Yield: 2.6 g of methyl acetate; b.p. 56-58°; n_D^{20} 1.3591; 6.5 g (51.2% of theory) of dimethyl malonate; b.p. 72-75° at 12 mm; n_D^{20} 1.4138; 2.5 g of monomethyl malonate (22% of theory); b.p. 145-148° at 50 mm (with decomposition).

Titration

0.0596 g of substance: 10 ml of 70% alcohol.

0.1N NaOH consumed in the cold	5.15 ml
Consumed after 15 minutes of boiling with excess alkali . . .	10.25 ml
$C_4H_6O_4$. Computed for neutralization	5.05 ml
Computed for neutralization and saponification	10.10 ml

Analysis of Silver Salt

Found %: Ag 48.05.

$C_4H_5O_4Ag$. Calculated %: Ag 48.00.

The substance isolated when the Ott's reagent is extracted with ether is recrystallized from a mixture of acetone and chloroform. M.p. 134-135°. A mixed sample with malonic acid fuses at 133.7-135°.

3. 10 g of finely powdered malonic acid is agitated with 40 g of acetic anhydride for 2 hours and then allowed to stand at room temperature for 24 hours. The malonic acid dissolves gradually, and the liquid turns yellowish brown with green fluorescence. The excess of acetic anhydride is driven off in vacuum at 50°, and 15 ml of absolute methanol is added drop by drop to the orange-brown sirupy mass that constitutes the residue. The reaction is so violent that chilling is required. Further treatment is like that in Exp. 1. Yield: 2.9 g of methyl acetate; b.p. 56-58°; n_D^{20} 1.3590; 7 g of dimethyl malonate (55.1%); b.p. 77-79° at 14 mm; n_D^{20} 1.3590; 2.4 g (21.1%) of monomethyl malonate; b.p. 145-149° at 50 mm (with decomposition).

Found %: C 40.63; H 5.44.
$C_4H_6O_4$. Calculated %: C 40.67; H 5.08.

4. 10 g of malonic acid and 40 g of acetic anhydride are heated over a water bath at 60-70° for 4 hours. The mixture is then treated as in the foregoing experiment.

Outwardly, the experiment differs from the preceding one solely in the more intense color. Yield: 2.7 g of methyl acetate; b.p. 56-58°; n_D^{20} 1.3596; 6.5 g of dimethyl malonate (51.6%); b.p. 77-80° at 13 mm; n_D^{20} 1.4144; 2 g of monomethylmalonate (17.6%); b.p. 144-150° at 50 mm (with decomposition).

5. 12.8 g of the neutral silver salt of malonic acid is added to 10 ml of absolute ether, and 6.3 g of acetyl chloride is added drop by drop with constant stirring. The ensuing reaction is very violent, and the liquid turns yellow. After cooling, the precipitate of silver chloride is filtered out and washed with absolute ether; the wash liquor is added to the main filtrate, and 2.5 g of absolute methanol is poured into the combined filtrate. Much heat is evolved. After cooling, the ether is driven off, and the residue is distilled in vacuum. B.p. 77-79° at 14 mm; n_D^{20} 1.4141. Yield of dimethyl malonate: 4 g (93.5% of theory).

6. 8.4 g of the acid silver salt of malonic acid is added to 10 ml of absolute ether, and then 3.1 g of acetyl chloride is added drop by drop with constant stirring. Further treatment as in the preceding experiment. After cooling, the reaction mass is treated with a 10% solution of soda. The ether solution is washed and dried; after the ether has been driven off, we get 0.4 g (13.5% of theory, based on the acetyl chloride) of methyl acetate with a b.p. of 55-58°; n_D^{20} 1.3598. The soda solution is acidulated with 25% sulfuric acid and extracted with ether; the ether solution is washed with water, dried, decolorized with activated charcoal, and distilled in vacuum after the ether has been driven off. B.p. 145-150° at 50 mm (with decomposition). Yield of monomethyl malonate: 4 g (84.7%).

Titration

0.1064 g of substance: 10 ml of 70% alcohol	
0.1 N NaOH consumed in the cold	9.11 ml
Consumed after 15-minute boiling with excess alkali	18.10 ml
$C_4H_6O_4$. Computed for neutralization	9.01 ml
Computed for neutralization and saponification	18.03 ml

Analysis of Silver Salt

Found %: Ag 47.86
$C_4H_5O_4Ag$. Calculated %: Ag 48.00

Synthesis of Mono- and Di-n-butyl Malonates

7. To the primary mixed anhydride, prepared from 10 g of malonic acid (Experiment 3), there is added 20 g of n-butyl alcohol. The reaction mass heats up considerably. Crystallization soon sets in. After it cools, the precipitate is filtered out, washed with ether, and recrystallized from a mixture of acetone and chloroform. 2.7 g of a white crystalline substance is recovered, with a m.p. of 132-134°. A mixed test sample with malonic acid fuses at 132.5-135°. The ethereal mother liquor is treated with a solution of sodium bicarbonate. The soda solution is then acidulated with 25% sulfuric acid, extracted

with ether, washed with water, dried, and decolorized with activated charcoal, after which the ether is driven off. Yield: 6 g (39% of theory) of a colorless oily liquid – mono-n-butyl malonate.

Titration

0.0795 g of substance: 10 ml 70% alcohol
0.1N NaOH consumed in the cold . . . . . 5.1 ml
Consumed after 3 hours of boiling with excess alkali . . . . . 9.7 ml
$C_7H_{12}O_4$. Computed for neutralization 4.95ml
Computed for neutralization and saponification . . . . 9.9 ml

Analysis of Silver Salt

Found %: Ag 40.55.
$C_7H_{11}O_4Ag$. Calculated %: Ag 40.45.

Mono-n-butyl malonate is decarboxylized by heat, a 120-130° fraction being driven off. After redistillation the b.p. is 123-126° (n-butyl acetate boils at 124-125°).

After the ether solution has been treated with soda, it is washed with water, dried, and – after the ether has been driven off – distilled. The following fractions were collected:

a) B.p. 123-126°: 3.5 g – n-butyl acetate.

b) B.p. 250-255°: 3 g (14.5% of theory) – n-dibutyl malonate (252°).

Synthesis of Mono- and Di-tert-butyl Malonates

8. The experiment is carried out as was the preceding one, using 12 g of trimethyl carbinol. Yield: a) 2.6 g of malonic acid with a m.p. of 132-134°, causing no depression when mixed with the initial malonic acid; and b) 5.5 g of mono-tert-butyl malonate (35.7% of theory).

Titration

0.1905 g of substance: 10 ml of 70% alcohol
0.1N NaOH consumed in the cold . . . . . 12.0 ml
Consumed after 4 hours of heating with excess alkali . . . . 23.8 ml
$C_7H_{12}O_4$. Computed for neutralization . . . . . 11.9 ml
Computed for neutralization and saponification . . . 23.8 ml

Analysis of Silver Salt

Found %: Ag 40.33
$C_7H_{11}O_4Ag$. Calculated %: Ag 40.45.

b) Di-tert-butyl malonate: 3 g (14.5% of theory); b.p. 220-225° with partial decomposition (di-tert-butyl malonate boils at 224°).

Saponification

0.2510 g of substance is boiled for 3 hours with an excess of 0.1N solution of alkali.
Consumption of alkali solution . . . . . 23.35 ml
$C_{11}H_{20}O_4$. Computed for saponification . . . . . 23.24 ml.

c) Tert-butyl acetate: 1 g; b.p. 94-96° (b.p. of tert-butyl acetate: 95°).

Synthesis of Mono- and Di-sec-octyl Malonates

9. The experiment is run along lines similar to those of the preceding one using 25 g of octanol-2. Yield: a) 2.2 g of malonic acid; m.p. 133.5-135.5°; b) 0.5 g of sec-octyl acetate; b.p. 190-193°; n_D^{20} 1.4143 (sec-octyl acetate boils at 193° ; n_D^{20} 1.4141); c) 5 g of di-sec-octyl malonate (15.9% of theory); b.p. 169-170° at 2mm; n_D^{20} 1.4367.

Saponification

0.5612 g substance: 25 ml of alcohol, boiled for 4 hours with excess of 0.1N solution of alkali.

Alkali consumed	3.4 ml
$C_{19}H_{36}O_4$. Computed for saponification	3.42 ml.

d) 3 g of mono-sec-octyl malonate (14.5% of theory).

Titration

0.0674 g of substance: 10 ml of 70% alcohol.

0.1N NaOH consumed in the cold	3.18 ml
Consumed in boiling for 2.5 hours with excess alkali . .	6.3 ml
$C_{11}H_{20}O_4$. Computed for neutralization	3.12 ml
Computed for neutralization and saponification	6.24 ml.

Synthesis of Mono- and Dilaurynyl Malonates

10. The experiment is performed as was the preceding one, using 35 g of lauryl alcohol. Yield: a) 3.5 g of malonic acid; m.p. 134-134.5°; b) 4 g of laurynyl acetate with a b.p. of 149-152° at 15 mm (151° at 15 mm); c) 7 g of dilauryl malonate (16.5% of theory) with a m.p. 33-34°.

Found %: C 73.35; H 11.60.
$C_{27}H_{52}O_4$. Calculated %: C 73.63; H 11.81.

d) 6 g of monolaurynyl malonate (23% of theory) with a b.p. of 42-43° (from diisoamyl ether). A mixed sample with the initial lauryl alcohol fuses without a temperature rise.

Titration

0.1028 g substance: 15 ml 80% alcohol.

0.1N NaOH consumed in the cold	3.64 ml
Consumed after 2 hours of heating with excess alkali . . .	7.43 ml
$C_{15}H_{28}O_4$. Computed for neutralization	3.77 ml
Computed for neutralization and saponification	7.54 ml

Found %: C 66.67; H 10.42.
$C_{14}H_{28}O_4$. Calculated %: C 66.17; H 10.29.

Synthesis of Mono- and Diphenyl Malonates

11. The experiment was run like the preceding one, using 20 g of fused freshly prepared phenol. Output: a) about 3 g of malonic acid, m.p. 134-135°; b) 4 g of phenyl acetate, m.p. 194-204°; n_D^{20} 1.5034 (m.p. 197°, n_D^{20} 1.5030); c) 4 g of diphenyl malonate (13.2% of theory), m.p. 49.5-51°; d) 3 g of monophenyl malonate (17.3% of theory), m.p. 65-66° (from diisoamyl ether).

Found %: C 59.89; H 4.65
$C_9H_8O_4$. Calculated %: C 60.00; H 4.44.

Titration

0.0449 g of substance: 10 ml of 70% alcohol.
0.1N NaOH consumed in the cold . . . . . 2.5 ml.
Consumed in 6 hours of heating with excess alkali . . . . . 4.98 ml.
$C_9H_8O_4$. Computed for neutralization . . . . . 2.47 ml.
Computed for neutralization and saponification . . . . 4.94 ml.

Analysis of the Silver Salt

Found %: Ag 37.73.
$C_9H_7O_4Ag$. Calculated %: Ag 37.63.

Synthesis of the Dianilide of Malonic Acid

12. To the primary mixed anhydride, prepared from 10 g of malonic acid (Exp. 3), 10 g of aniline is added. Extremely intense evolution of heat takes place, and after cooling the glassy reaction mass quickly crystallizes. Repeated recrystallizations from methanol and from a mixture of the latter with benzene yield 12 g (71% of theory) of the dianilide of malonic acid with a m.p. of 223-224.5°.

Kjeldahl Nitrogen Determination

Found %: N 11.39, 11.15.
$C_{15}H_{14}O_2N_2$. Calculated %: N 11.02.

Synthesis of the Mono- and Dianilides of Malonic Acid

13. To the primary mixed anhydride, prepared from 10 g of malonic acid, there is added a solution of 15 g of aniline in 25 ml of absolute ether. The ether starts to boil, and almost instantly a yellow deposit begins to settle out. Two hours later the deposit is filtered out and recrystallized from methanol. We get 12 g of the dianilide of malonic acid with a m.p. of 224-225°. The ether solution is partially evaporated, and the crystals obtained are fractionally recrystallized from a 4:1 mixture of benzene and methanol. This yields one more gram of the dianilide with a m.p. of 224-225° and 3 g of a white crystalline substance with a m.p. of 100-105°. The m.p. is 110-111° after another recrystallization from a 10:1 mixture of benzene and methanol, and is 114-115° after recrystallization from water. A mixed sample with acetanilide causes no depression. The ethereal mother liquor is treated with a solution of sodium bicarbonate. The soda solution is acidulated with 10% sulfuric acid and again extracted with ether. The ether extract is washed with water and dried, and the ether is driven off. Yield: 4.5 g of the monoanilide of malonic acid with a m.p. of 131-132° (from glacial acetic acid).

Titration

0.1512 g of substance: 20 ml of 70% alcohol.
0.1N NaOH consumed . . . . . 6.71 ml.
$C_9H_9O_3N$. Computed for neutralization . . . . . 6.78 ml.

Analysis of the Silver Salt

Found %: Ag 38.10.
$C_9H_8O_3Ag$. Calculated %: Ag 37.94.

Decarboxylation of the Monoanilide of Malonic Acid.

0.5 g of the monoanilide is heated to the melting point, and after

no more carbon dioxide is evolved and the mass has cooled, the residue is recrystallized from water. Yield: 0.4 g of acetanilide, m.p. 111-112°. A mixed sample with an analytical standard fuses at 109-112°.

Synthesis of a Mixed Anhydride of Monomethyl Malonate and Acetic Acid

14. To 5 g of monomethyl malonate, dissolved in 20 ml of acetic anhydride, 2 drops of concentrated sulfuric acid are added, causing the evolution of considerable heat. Twenty-four hours later excess acetic anhydride is driven off in vacuum at a bath temperature that does not exceed 50°, and the residue is fractionated in vacuum. A fraction with a b.p. of 64-65° at 5 mm or 70-71° at 7 mm is collected. The yield of the mixed anhydride of monomethyl malonate and acetic acid is 2 g (29.4% of theory); n_D^{20} 1.4106.

Found %: C 45.18; H 5.00.
$C_6H_8O_5$. Calculated %: C 45.0; H 5.00.

The odor of acetic acid begins to be noticed when the product is left standing exposed to air. It does not react with acetone.

Action of Methanol Upon the Mixed Anhydride

To 3 g of the freshly distilled mixed anhydride there is added 5 ml of absolute methanol, which is accompanied by some evolution of heat; upon cooling, the mixture is distilled. B.p. 177-181° (dimethylmalonate: 180°).

Saponification

0.2067 g of substance boiled for 1 hour with 0.1 N solution of NaOH.
Alkali solution consumed . . . . . 30.0 ml.
$C_5H_8O_4$. Computed for saponification . . . 30.32 ml.

Action of Aniline Upon the Mixed Anhydride

To 3 g of the freshly distilled mixed anhydride there is added 3 g of aniline; this causes the evolution of considerable heat. After cooling, the mixture is dissolved in ether and treated with 10% sulfuric acid to eliminate the excess aniline. The ether solution is washed with water and dried, after which the ether is driven off. Part of the residue crystallizes. It is treated with a solution of sodium bicarbonate and recrystallized from water. The yield is 0.4 g of pearly crystals with a m.p. of 110-111°.

A mixed sample with acetanilide fuses at 109-111°. The soda solution is acidulated with 10% sulfuric acid and extracted with ether, the ether extract is washed with water and dried, and the ether is driven off. Yield is 1 g of an oily substance: monomethyl malonate.

Titration

0.0864 g of substance
0.1N NaOH consumed . . . . . 7.45 ml.
$C_4H_6O_4$. Computed for neutralization . . . . 7.32 ml.

Reaction of the Mixed Anhydride with p-Nitrobenzyl Bromide

1 g of the mixed anhydride, 1.1 ml of a 10% solution of NaOH, 15 ml of 65% alcohol, and 1.35 g of p-nitrobenzyl bromide are boiled together for 1 hour over a water bath. After the reaction mass has cooled, an oil is removed from it; the oil soon crystallizes, m.p. 64-72°. Repeated fractional crystallizations from pure and 70% alcohol yield 2 fractions:

a) M.p. 78-79°; a mixed sample with p-nitrobenzyl acetate fuses at 77-79°.

b) M.p. 83-84°; a mixed sample with p-nitrobenzyl malonate fuses at 82.5-84°.

Synthesis of the Mixed Anhydride of Mono-n-butyl Malonate and Acetic Acid

15. 16 g of acetic anhydride is added to 4 g of mono-n-butyl malonate, and the mixture allowed to stand for 24 hours. The excess acetic anhydride is driven off in vacuum at a bath temperature that does not exceed 50°, and the residue is double-distilled in vacuum. B.p. 116-116° at 4 mm. Yield: 3 g (59.4% of theory).

Found %: C 53.29; H 7.10.
$C_9H_{14}O_5$. Calculated %: C 53.44; H 6.93.

The odor of acetic acid is noticed when the substance is allowed to stand exposed to the air.

Action of Aniline Upon the Mixed Anhydride

2 g of aniline is added to 1 g of the mixed anhydride. Considerable heat is evolved. After the mixture cools, it is dissolved in ether, the excess aniline is removed with 10% sulfuric acid, and the ether is driven off. The yield is a thick oil, part of which soon crystallizes. After a second recrystallization from water, the crystals fuse at 111.5-113°. A mixed sample with acetanilide fuses at 109.5-113°.

Synthesis of the Mixed Anhydride of Monophenyl Malonate and Acetic Acid

16. 5 g of acetic anhydride is added to 1 g of monophenyl malonate, and the mixture is allowed to stand for 24 hours. The excess acetic anhydride is driven off in vacuum. The residue is a yellow oil, part of which soon crystallizes. M.p. 49-51°. After double recrystallization from diisoamyl ether we get 0.7 g (56.9% of theory) of a white crystalline substance with a m.p. of 55.5-56°. A mixed sample with the initial monophenyl malonate fuses at 41-49°.

Found %: C 59.40; H 4.69.
$C_{11}H_{10}O_5$. Calculated %: C 59.46; H 4.56.

Action of Aniline on the Mixed Anhydride

0.5 g of aniline is added to a solution of 0.3 g of the mixed anhydride in 3 ml of diisoamyl ether. A white precipitate with a m.p. of 49-55° instantly settles out. It is dissolved in ether and treated with a solution of sodium bicarbonate. The residue after the ether has been driven off is a white crystalline substance with a m.p. of 113-114°, (from water). A mixed sample with acetanilide fuses at 113-114°. The soda solution is acidulated with 10% sulfuric acid, extracted with ether, and dried, and the ether driven off. The output is a white crystalline substance with a m.p. of 62-63°. A mixed sample with monophenyl malonate fuses at 61-62°.

Titration

0.1216 g substance: 10 ml of 70% alcohol.
Consumption of 0.1 N NaOH in the cold . . . . . 6.8 ml.
Consumed in 2 hours of heating with excess alkali . . . . 13.6 ml.

$C_9H_8O_4$. Computed for neutralization . . . . . 6.75 ml.
Computed for neutralization and saponification 13.51 ml.

SUMMARY

1. It has been established that when malonic acid is reacted with acetic anhydride there are formed two mixed anhydrides (the acid and the neutral) of malonic and acetic acids. Sulfuric acid acts only as a catalyst in this process.

2. These mixed anhydrides can be synthesized by the classic reaction of anhydride formation: the reaction of a silver salt of malonic acid (acid or neutral with acetyl chloride.

3. The acid esters of malonic acid likewise yield mixed anhydrides with acetic anhydride; these mixed anhydrides can be isolated in a chemically pure state.

4. All the synthesized mixed anhydrides yield a mixture of ethers with alcohols, and anilides of acetic and malonic acids when reacted with aniline.

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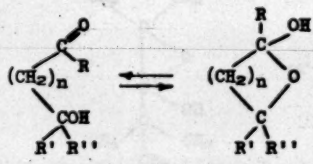
RESEARCH IN THE FIELD OF CYCLIC ACETALS OF HYDROXY CARBONYL COMPOUNDS

I. SYNTHESIS AND PROPERTIES OF THE METHYL LACTOLIDE OF METHYLBENZOYLCARBINOL (1-METHOXY-1-PHENYL-PROPENE-1-OXIDE).

T. I. Temnikova and E. N. Kropacheva
A. A. Zhdanov Chair of the Structure of Organic Compounds, Leningrad State University, awarded the Order of Lenin

Intramolecular reaction between the hydroxyl and carbonyl groups in hydroxy carbonyl compounds may result in the formation of cyclic compounds that are intramolecular hemiacetals. The transition from the open-chain to the cyclic form is reversible; the equilibrium status depends on a number of factors [1]:



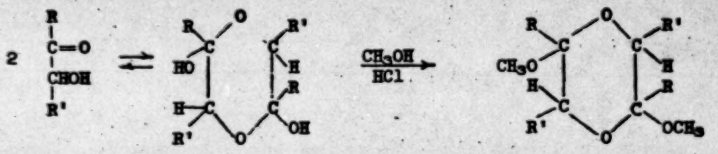
The stability of the cyclic form depends principally on the magnitude of the ring: compounds containing five-membered or six-membered rings are stable and are easily formed from the corresponding γ- or δ-hydroxy carbonyl compounds, especially when the latter are hydroxy aldehydes.

If the equilibrium position is shifted to the left, as is the case in the hydroxy ketones, the presence of even an infinitesimal amount of the cyclic form can be proved by conversion into a methyl acetal (methyl lactolide) under the action of methanol and HCl [2].

In the α-hydroxy carbonyl compounds the question of possible intramolecular reaction between these groups, forming a strained three-membered oxide ring:

cannot be considered as settled up to now.

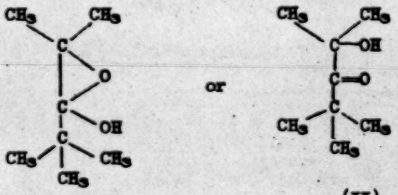
In the free state, α-hydroxy aldehydes, hydroxyacetone, and dihydroxyacetone form dimeric molecules [3] as a result of the intramolecular reaction between the carbonyl and hydroxyl groups of two molecules. When methanol acts upon an α-hydroxy carbonyl compound in the presence of HCl, we get the methyl ethers of the substituted dioxydioxane [4]:



But no conclusion can be arrived at from these data alone as to whether oxotautomerism occurs in α-hydroxy carbonyl compounds as the result of the intramolecular reaction of the carbonyl and hydroxyl groups.

An alcoholo-oxide structure is assumed for the substance first isolated by A.M.Butlerov among the oxidation products of diisobutylene and called oxoctenol by him [5].

A.M.Butlerov suggested two equally probable formulas (I) and (II) for this compound:



(I) (II)

The negative result of the reaction with hydroxylamine led Meyer and Nageli [6] to accord preference to the first formula. It should be noted, however, that the subsequent research of N.A.Prilezhayev [7] on oxoctenol does not make it possible to decide unequivocally in favor of either one of the formulas proposed by A.M Butlerov. Analogues of oxoctenol were synthesized by A.M.Khatsky [8] and also described as alcoholo-oxides.

It was to be expected that the alkoxide rings of the foregoing type of structure would not be stable; in any event this might be supposed for compounds in which supplementary intramolecular reactions could not bring about the stabilization of the oxide structure.

We reach this conclusion when we bear in mind that cyclopropanol, which contains a three-carbon ring, i.e., is more stable than the oxide, cannot be obtained.

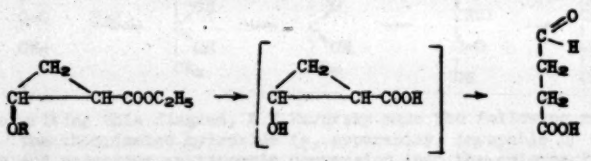
According to N.M.Kizhner, cyclopropanol should isomerize to propionaldehyde: [9]

The possibility of the reaction following this course was confirmed by Lipp [10], who demonstrated the spontaneous isomerization of the apotricyclol he had synthesized to camphenylol:

Transformation of both the alcohol oxide and the cyclo-propanol into open-chain forms should, in my opinion, take place as the result of the migration of hydrogen via an ionic mechanism. Hence, it is to be expected that replacement of the hydrogen by alkyl or acyl groups could yield compounds possessing high stability and capable of independent existence.

And, indeed, I.A.Dyakonov [11] has succeeded in synthesizing and describing the ethyl esters of ethoxy-, butoxy-, and acetoxycyclopropanecarboxylic acids.

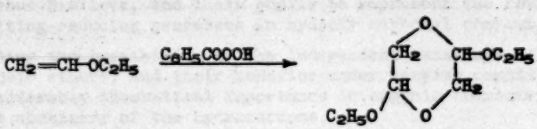
When we endeavored to make the transition to cyclopropanolcarboxylic acid, isomerization was observed, with the formation of succinic aldehyde:



where R = C_2H_5, C_4H_9, or $COCH_3$.

Examination of the literature dealing with compounds containing an alkoxy group at the oxide ring yields no definite decision on the viability of this type of compound.

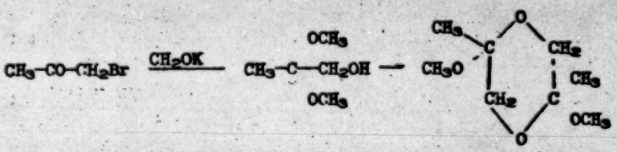
Bergmann and Miekeley [12] tried to synthesize a compound containing an ethoxy group at the oxide ring by oxidizing the ethyl vinyl ether of benzoyl hydrogen peroxide. But, instead of the expected acetal he got a dimerization product:



By allowing sodium methylate to act on desyl chloride Madelung and Oberwegner [13] obtained a substance, the structure of which they assumed included an oxide ring:

Their description of the chemical transformations, however, was so inaccurate that it is impossible to draw definite conclusions concerning the

correctness of the formulas proposed by them. It is of interest to note that Bergmann and Miekeley [14], in an analogous reaction starting with bromacetone, obtained an ether of dioxydioxane; they isolated the dimethyl acetal of hydroxy acetone:



as an intermediate product.

A.E.Favorsky assumed the formation of monomolecular internal hemiacetals of the β-hydroxy carbonyl compounds as the schematic representation of the course of the isomeric transformations of hydroxy carbonyl and halogen carbonyl compounds. In his doctoral dissertation, discussing the possible course of the process of synthesizing the acids of the acrylic series from the dichloroketones, A.E.Favorsky was the first to propose a diagram in which an oxide ring takes part:

In writing this diagram, E.E.Favorsky made the following reservation, however: "the chlorinated hydroxide is, apparently, incapable of independent existence and undergoes an isomeric conversion into the chloroacid at the instant of its formation."

The question of the formation of alcohol-oxide rings in a transitional state during chemical reactions, i.e., under conditions where the molecular state is richer in energy, represents a problem all by itself; this latter problem can be solved only after study of the conditions and the nature of the transformations of oxide rings of this type in suitable compounds.

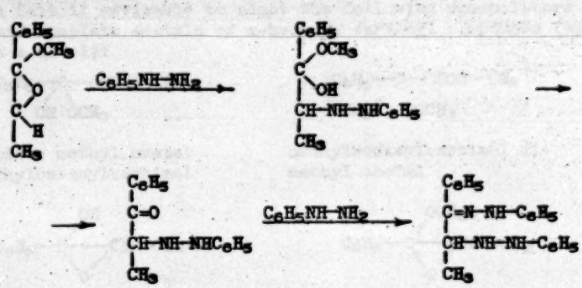
Later, alcohol-oxide diagrams were propounded by A.E.Favorsky, S.N. Danilov, E.D.Venus-Danilova, and their pupils to represent the course of intramolecular oxidizing-reducing processes in hydroxy carbonyl compounds [18].

Elucidating the possibility of the independent existence of alcohol oxides or of their ethers, and their behavior under varying conditions is a problem of considerable theoretical importance in organic chemistry and, in particular, the chemistry of the hydrocarbons.

In effecting the reaction between α-bromoethylphenyl ketone and anhydrous sodium methylate in an absolute-ether medium, we succeeded in obtaining a compound containing an oxide ring with a methoxyl group attached to the carbon ring, (1-methoxy-1-phenylpropene-1 oxide). The substance, isolated by vacuum distillation, proved to be very unstable, polymerizing noticeably within as little as 12 hours. The substance possesses the properties of an oxide: it slowly liberates iodine from a KI solution; when it reacts with bromophenylmagnesium, considerable diphenyl is formed, which also indicates the oxidizing properties of the substance.

When it is heated with Fehling solution, cuprous oxide is very slowly precipitated. Dissolving it in methanol gives rise to intensive heating, even causing the alcohol to boil up, and forming a new product; this latter is the subject of further investigation.

When it is reacted with phenylhydrazine, we get a colorless crystalline substance that contains two phenylhydrazine radicals; we are of the opinion that it is the phenylhydrazidophenylhydrazone of methylbenzoylcarbinol, formed as follows:



To demonstrate the presence of an oxide bond and of a methoxy group attached to the carbon atom linked to the phenyl group, we hydrolyzed the substance by heating it with 5% sulfuric acid. Hydrolysis yielded methylbenzoylcarbinol.

It should be noted however, that only after a series of experiments were we able to manage the process in such a way as to cause neither polymerization of the oxide nor its isomerization nor an isomeric conversion of the initially formed methylbenzoylcarbinol into the more stable phenylacetylcarbinol.

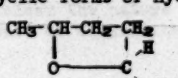
When all the experimental data are compared (cf. the diagram on p. a 389), it is safe to say that the substance we synthesized has an alkoxy group and is a complete cyclic acetal of methylbenzoylcarbinol.

Before proceeding with the further discussion of our research, we must dwell upon problems of nomenclature.

Our research enables us to state that there are two types of cyclic acetals for α-hydroxycarbonyl compounds: the monomolecular, which can be synthesized indirectly from the bromoketones; and the bimolecular, which are formed from α-hydroxy carbonyl compounds under ordinary conditions (CH_3OH + HCl); these acetals are ethers of substituted dioxydioxanes.

The nomenclature of the two types of acetals has to be worked out.

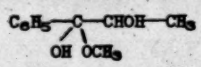
By analogy with the lactones, Helferich and Fries suggested the name "lactols" [17] for the cyclic forms of hydroxy carbonyl compounds, viz:



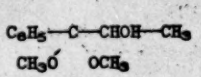
Lactol of γ-hydroxybutyraldehyde (γ-lactol)

The name "methyl lactolide" was proposed for the methyl ethers of the lactols, which are complete cyclic acetals of hydroxy carbonyl compounds.

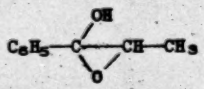
For the α-hydroxy carbonyl compounds, however, the latter name was given to the substances obtained in the reaction with methanol in the presence of HCl, which have a double structure and are derivatives of dioxydioxane [18]. It is evident that a name of this sort is incorrect for such compounds. The complete cyclic acetals of the type of our compound should be called methyl lactolides of α-hydroxy carbonyl compounds, since they are true derivatives of the lactol forms. We felt it advisable to adopt the following nomenclature for the incomplete and complete acetals of α-hydroxy carbonyl compounds (using our ketonic alcohol as a model):



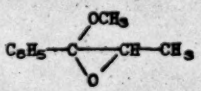
incomplete methyl acetal of methylbenzoylcarbinol



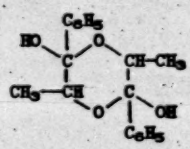
methylbenzoylcarbinol dimethyl acetal



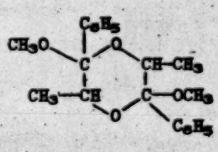
methylbenzoylcarbinol lactol



methylbenzoylcarbinol methyl lactolide

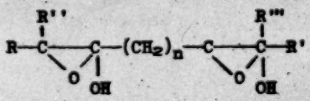


methylbenzoylcarbinol cyclodilactol



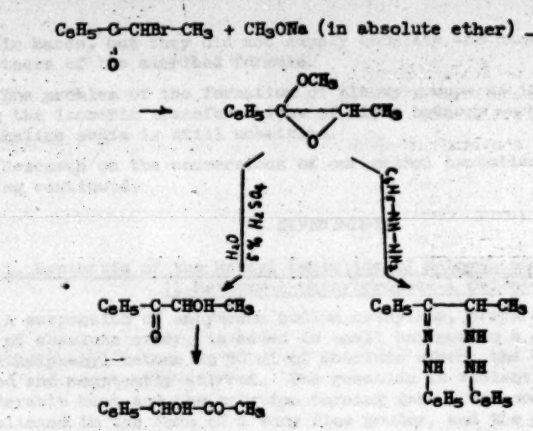
methylbenzoylcarbinolcyclodimethyldilactol

Addition of the prefix "cyclo" is necessary to distinguish them from the dilactols, which are open-chain in form: derivatives of dihydroxydicarbonyl compounds:

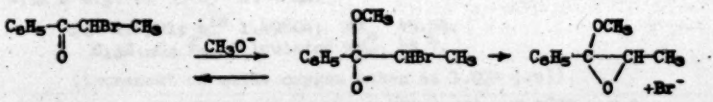


To call cyclodilactols substituted dioxydioxanes would be inconvenient, since their chemical behavior is governed by the fact that they are acetals. The term bimolecular or "dimeric methyl lactolide" [18] is inaccurate, since the name does not make clear the nature of the dimerism. Thus, the substance we have synthesized should be called the methyl lactolide of methylbenzoylcarbinol.

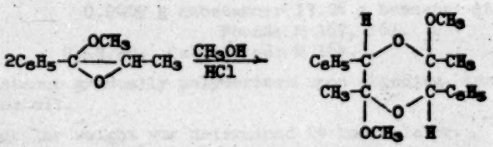
The results of our research may be pictured by the following diagram:



The formation of methylbenzoylcarbinol methyl lactolide may be represented by the following diagram:



When the methyl lactolide is added to methanol containing 3% hydrogen chloride, the solution is observed to warm up considerably; crystals that are practically insoluble in methanol are precipitated at once. After being dried and recrystallized from benzene, the substance is obtained in the form of a fine powder with a m.p. of 251° in a sealed capillary, which is characteristic of the cyclodimethyldilactolide of phenylacetylcarbinol [4]. A mixed test sample made with a standard sample fused at the same temperature.



The extreme instability of the methylbenzoylcarbinol methyl lactolide synthesized by us, its easy isomerization in the presence of acid reagents, and its activity even with alcohol explain why previous researchers failed to synthesize this type of compound. Bergmann and Miekeley, after reacting benzoyl hydrogen peroxide with ethylvinyl ether, subjected the reaction product to distillation in the presence of benzoic acid [12]. In another paper [14] they effected the reaction in the presence of alcohol. In both cases they obtained the products of the further conversion of the substance under their experimental conditions.

Madelung and Oberwegner [13] possibly had the methyl lactolide of benzoin

in their hands, but they did not supply complete and convincing proofs of the correctness of the ascribed formula.

The problem of the formation of alkoxy groups as intermediate products during the isomeric transformations of alpha hydroxy carbonyl compounds in acid and alkaline media is still unsettled.

Research on the conversions of our methyl lactolide under various conditions is being continued.

EXPERIMENTAL

1. Synthesis of the Methyl Lactolide of Methylbenzoylcarbinol (1-Methoxy-1-phenylpropene-1 Oxide).

A suspension of anhydrous sodium methylate, prepared from 10 g of Na in 60 ml of absolute ether, is added in small batches to a solution of 32 g of α-bromoethylphenyl ketone in 50 ml of absolute ether, the whole being carefully chilled and constantly stirred. The reaction is violent, with the evolution of considerable heat and the solution turning dark. The sodium bromide, which is precipitated in the form of a very fine powder, and the excess sodium methylate, are passed through a porous suction filter; the ether is driven off from the filtrate; and the residue is distilled in vacuum. Yield: 10 g of a mobile liquid with a b.p. of 63-65° at 4 mm.

d_4^{19} 1.0521; n_α^{19} 1.49604; MR_α 45.54.
$C_{10}H_{12}O_2$ F_3. Calculated MR_α 45.7.

(increment of oxide oxygen taken as 1.074 [19])

0.1043 g substance: 0.2799 g CO_2; 0.0690 g H_2O.
0.1207 g substance: 0.3168 g CO_2; 0.0778 g H_2O.
Found %: C 73.18, 73.13; H 7.40, 7.21.
$C_{10}H_{12}O_2$. Calculated %: C 73.17; H 7.31.

0.1516 g substance: 0.2130 g AgI.
Found %: OCH_3 18.65
$C_9H_9O(OCH_3)$. Calculated %: OCH_3 18.90.

0.1496 g substance: 17.26 g benzene: Δt 0.265°.
0.2009 g substance: 17.26 g benzene: Δt 0.369°.
Found: M 167, 161.
$C_{10}H_{12}O_2$. Calculated: M 164.

The substance gradually polymerizes upon standing, turning into a less mobile, viscous oil.

The molecular weight was determined 24 hours later.

0.909 g substance; 15.2 g benzene: Δt 0.100°.
Found: M 303.9.

II. Reaction of the Methyl Lactolide of Methylbenzoylcarbinol with Phenylhydrazine

A solution of 1.5 g of phenylhydrazine in 4.5 ml of ethyl alcohol containing a few drops of glacial acetic acid is added to 0.5 g of the methyl lactolide. After being heated for 30 minutes over a water bath, the solution was allowed to stand overnight. The next day white crystals settled out; they were washed with alcohol, acetic acid, water, and again alcohol. Recrystallization from alcohol

yielded a colorless substance with a m.p. of 126°. Yield: 0.45 g.

0.0738 g substance: 11.1 ml N_2 (22.5°, 758 mm)
0.0547 g substance: 8.2 ml N_2 (17°, 753.2 mm).
Found %: N 17.09, 17.05.
$C_{21}H_{22}N_4$. Calculated %: N 16.95.

0.0800 g substance: 20.01 g benzene: Δt 0.060°.
Found: M 341.
$C_{21}H_{22}N_4$. Calculated: M 330.

Upon standing, the surface of the substance turns yellow, but recrystallization from alcohol yields colorless crystals again.

III. Hydrolysis of the Methyl Lactolide of Methylbenzoylcarbinol

Endeavors to hydrolyze the methyl lactolide with sulfuric acid of varying concentrations or by moderate heating covert most of it into a viscous polymer, with the formation of a small amount of a crystalline substance with a m.p. of 208°.

Hydrolysis of the methyl lactolide succeeded under the following conditions:

1) To 3 g of the substance there was added 100 ml of 5% sulfuric acid, and the mixture was heated, with stirring, over a water bath and with a reflux condenser. The substance gradually dissolved, and a small quantity of white crystals appeared on the surface. The latter were removed and washed with petroleum ether. Yield: 0.04 g with a m.p. of 208°.

0.0106 g substance: 0.1004 g camphor: Δt 13.2°
Found: M 320.5.
$C_{20}H_{24}O_4$. Calculated: M 328.

The aqueous solution was extracted with ether, the ether extract was dried with $MgSO_4$, and the ether was driven off. The residue was distilled in vacuum. The yield was 1.5 g of a slightly yellowish, mobile liquid with a b.p. of 120-121° at 12 mm; n_α^{17} 1.52947.

The substance yielded a semicarbazone with a m.p. of 189°, which exhibited no depression of the melting point when mixed with a standard preparation of the semicarbazone of phenylacetylcarbinol.

The following constants are given in the literature for phenylacetylcarbinol: b.p. 126-126.5° at 15 mm; $n_\alpha^{16.5}$ 1.53132; semicarbazone, m.p. 189° [20].

2) 8.5 g of the methyl lactolide was added in small batches to 5% sulfuric acid, heated to 80°. The reaction was continued for an hour and a half over a boiling water bath, with constant stirring. The reaction product was extracted with ether, and the ether extract washed with soda. After the ether was driven off, the residue was distilled in vacuum. The yield was 3.43 g of a substance with a b.p. of 83-85° at 1.5 mm; n_α^{19} 1.54571. Allowing it to stand with a water-alcohol solution of semicarbazide yielded a colorless crystalline substance with a m.p. of 230°, which agrees with the data reported by Auwers, according to whom methylbenzoyl carbinol yields the disemicarbazone of acetylbenzoyl when allowed to stand for a long time in a semicarbazide solution [21].

Reaction of the hydrolysis product with bromophenylmagnesium. The reaction was effected by the method described earlier [22], using 2.6 g of magnesium, 16 g of bromobenzene, and 3 g of the substance produced by hydrolysis. The substance isolated (3.85 g) was recrystallized from petroleum ether; it fused at 91-92°.

The substance did not contain a methoxy group.

0.0935 g substance: 0.2717 g CO_2; 0.0619 g H_2O.
Found %: C 79.25; H 7.41.
$C_{15}H_{16}O_2$. Calculated %: C 78.91; H 7.07.

The melting point and the analysis of the substance identified it as 1,1-diphenylpropanediol-1,2.

Oxidation of the glycol. 1.33 g of CrO_3 in 20 ml of water was added in one batch to a mixture of 2 g of the glycol and 5 g of $KHSO_4$ in 10 ml of H_2O. Oxidation was effected by the method described previously. Output: 1 g of benzophenone with a m.p. of 47°, a mixed sample with standard benzophenone not exhibiting any depression. The benzophenone obtained by this oxidation was identified as the phenylhydrazone, with a m.p. of 136°, which also exhibited no depression of the melting point when mixed with the phenylhydrazone of benzophenone.

IV. Reaction of the Methyl Lactolide of Methylbenzoylcarbinol with Methanol and HCl

3 ml of 3% HCl in methanol was added to 0.5 g of the methyl lactolide. The liquid boiled up violently, white crystals that were insoluble in the methanol separating out throughout the mixture. The substance, recrystallized from benzene, fused at 251°. Yield: 0.3 g. A sample, when mixed with the cyclodimethyldilactolide of phenylacetylcarbinol (2,5-dimethoxy-2,5-dimethyl-3,6-diphenyldioxane) fused at the same temperature [4].

SUMMARY

1. The reaction of α-bromoethylphenyl ketone with sodium methylate in anhydrous ether yielded the methyl lactolide of methylbenzoylcarbinol (1-methoxy-1-phenylpropene-1-oxide).

2. The structure of the substance was proved by its hydrolysis to methyl benzoylcarbinol and by its reaction with phenylhydrazine to form the phenylhydrazidophenylhydrazone of methylbenzoylcarbinol.

3. The methyllactolide of methylbenzoylcarbinol is highly unstable: it polymerizes easily upon standing, is subject to various isomeric transformations when acted upon by acid agents, and undergoes change when dissolved in alcohol.

4. When acted upon by HCl in methanol, the methyl lactolide of methylbenzoylcarbinol is converted into the cyclo-dimethyldilactolide of phenylacetylcarbinol (2,5-dimethoxy-2,5-dimethyl-3,6-diphenyl-1,4-dioxane).

5. Nomenclature is proposed for various types of acetals of α-hydroxy carbonyl compounds.

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*See CB translation p.173a

THE REACTIONS OF SULFUR WITH UNSATURATED COMPOUNDS

IV. PHENYL-SUBSTITUTED 1,1-DITHIOL-3-THIONES

M. G. Voronkov, A. C. Broun* and G. N. Karpenko

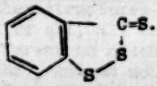
Chair of Organic Chemistry, Leningrad State University awarded the Order of Lenin

Two of the present authors have already reported [1,2], their discovery in 1944 of a new development in the sulfurizing reaction of unsaturated compounds,** resulting in the formation of derivatives of 1,2-dithiol-3-thione.***

where R_1, R_2 = alkyl, aryl H.

In the present paper we shall deal in detail with the synthesis and the proof of the structure and properties of the phenyl-substituted dithiolthiones.

Up to the present time only one compound containing the dithiolthione group has been described in the literature. This is the so-called "dithiosulfidene" (4,5-benzo-1,2-dithiol-3-thione):



It was synthesized by letting phosphorus pentasulfide act upon saccharin, the latter's sodium salt, thiosaccharin [3 4], or o-mercaptobenzoic disulfide [5,6]. Moreover, one oxygen analogue of the dithiolthione derivatives has been known. This is 5-phenyl-1,2-dithiol-3-one, which is easily synthesized by the action of sulfur upon the ethyl ester of cinnamic acid [7]:

In our study of the reactions of sulfur with unsaturated compounds [1,2 8-10], we sulfurized phenyl olefins with various numbers and positions of the phenyl groups and double bonds and with different structure of the aliphatic

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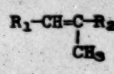
* Deceased

** Cf. [1] for an exhaustive survey of the literature on the action of sulfur upon unsaturated compounds (a bibliography with more than 400 entries).

*** According to Patterson [8].

radical. It was shown that, of the large number of hydrocarbons investigated in this respect, those having the structure of phenyl-substituted propenes:

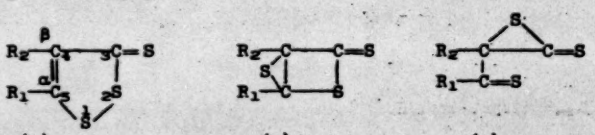


where R_1 = H, C_6H_5; R_2 = H, CH_3, C_6H_5 (one of the radicals is always C_6H_5).

react with sulfur in a single manner, forming sulfur compounds that resemble one another in composition, chemical properties, and even external appearance.

We investigated the reaction of sulfur with 1-phenylpropene-1, 2-phenylpropene-1, 2-methyl-1-phenylpropene-1, and 1,2-diphenylpropene-1 at high temperatures (160-250°). A reaction takes place with all of these phenyl olefins involving the introduction of three atoms of sulfur into the molecule of the initial hydrocarbon and the cleavage of four hydrogen atoms as hydrogen sulfide. When the sulfur compounds thus formed are oxidized with dilute nitric acid or hydrogen peroxide, we always get benzoic acid (together with sulfuric acid). This excludes the possibility that the sulfur enters the aromatic ring.

Thus, sulfuration reaction of the phenyl olefins of the foregoing type yields the aromatic sulfur compounds $R_1R_2C_3S_3$, containing the characteristic $>C_3S_3$ group. The only possible structures for this group are the three following ones:



(A) (B) (C)

where R_1 = H, C_6H_5; R_2 = H, CH_3, C_6H_5 (one of the radicals is always C_6H_5).

The chemical properties of the compounds synthesized compel us to assume for them the structure of derivatives of 1,2-dithiol-3-thione (A) and to reject beyond doubt the two other structures (B) and (C), which are, moreover, improbable sterically. First of all, all the foregoing compounds are monomolecular, thermally stable, indifferent to alcoholic bases, boiling water, and concentrated acids (HCl and HBr), and do not polymerize under any conditions. This points to the absence of an ethylene-sulfide ring, present in structures (B) and (C), in their molecules.* The synthesized compounds contain a single thioketone group, as they form mono-oximes with hydroxylamine, liberating hydrogen sulfide. They contain no active hydrogen, as they do not liberate methane with methylmagnesium iodide and do not react with metallic sodium. When acted upon by aqueous alkalies, they first form compounds that contain a free sulfhydryl group, as is proved by the characteristic dark-red color imparted to it by the Grothe reagent (alkali + sodium nitroprusside) that is specific for this group. When acted upon by aqueous alkalies at high temperatures, they are cleaved, forming benzoic acid. This indicates the presence of a disulfide group, in which there are double bonds alongside the sulfur [12], one sulfur atom being attached to the carbon atom that is directly linked with the aromatic ring. The conjectural mechanism of the reaction with an aqueous alkali may be represented by the following diagram:

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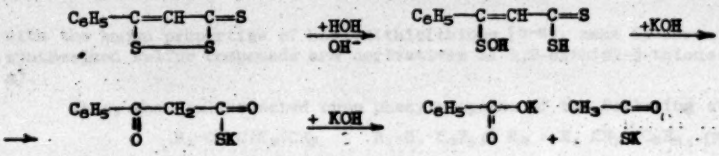
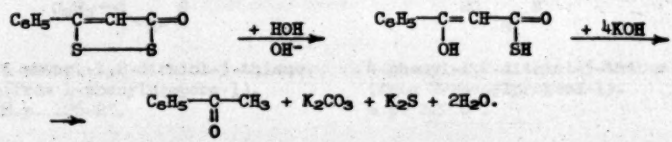
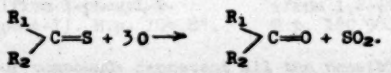
* It is known [11] that compounds containing the ethylene-sulfide group are extremely unstable, highly prone to polymerize, and highly sensitive to various reagents (especially to bases.)



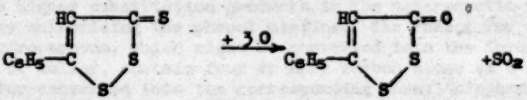
An interesting circumstance is the fact that α-phenyldithiolone is cleaved by an alkali in a different manner [7]:*



When the synthesized compounds are oxidized by permanganate under mild conditions, one sulfur atom is replaced by oxygen. This indicates that the latter sulfur atom is not equivalent to the other two, entering into the thioketone grouping, since the thioketones are oxidized in exactly this manner [13]:



Thus, the oxidation reaction apparently follows this course:



The oxidation product of α-phenyldithiolthione synthesized by us in accordance with the foregoing equation is identical with α-phenyldithiolone [7] in melting point, crystalline form, analytical data, and molecular-weight determination, differing somewhat from it only in the matter of color (pale red instead of yellow). It is possible that the latter factor is due to a slight admixture of the unoxidized sulfurous analogue, which possesses a highly intensive coloring action.

The compounds we synthesized are readily reduced by sodium in isoamyl alcohol or by zinc in formic or acetic acid. They very easily form poorly soluble addition compounds with the halogens and the salts (chiefly the halides) of the heavy metals (Hg, Zn, Cd, Au, Cu, Sb, Fe, Pt, and Pd). The reaction with an excess of methyl iodide, which occurs very easily, results in the formation of iodomethylates — orange or red crystalline substances that are insoluble in ordinary organic solvents. Their structure is still obscure, and we shall not dwell upon them here. The cited data, together with the data of X-ray investigation [14], as well as the resemblance of their chemical properties

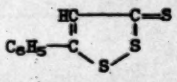
* It may be assumed that when phenylated 1,2-dithiol-3-thiones are acted upon by alkalies, they are decomposed to some degree along these lines. The aromatic ketones formed thereby were detected solely by their odors, however.

with the known properties of benzodithiolthione [3-8], make it certain that the synthesized sulfur compounds are derivatives of 1,2-dithiol-3-thione (Structure A).

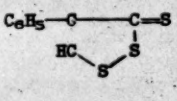
Thus, when sulfur acted upon phenylpropenes of the following structure:

R_1–CH=C(R_2)CH_3 R_1=H, C_6H_5; R_2 = H, CH_3, C_6H_5; (R_1,R_2 = phenyl)

we obtained the following derivatives of 1,2-dithiol-3-thione:

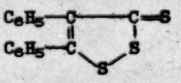


5-phenyl-1,2-dithiol-3-thione (from 1-phenylpropene-1). M.p. 126.2°.



4-phenyl-1,2-dithiol-3-thione (from 2-phenylpropene-1). m.p. 122.8°.

4-methyl-5-phenyl-1,2-dithiol-3-thione (from 1-phenyl-2-methylpropene-1). M.p. 104.6°.



4,5-diphenyl-1,2-dithiol-3-thione (from 1,2-diphenylpropene-1). M.p. 160.5°.

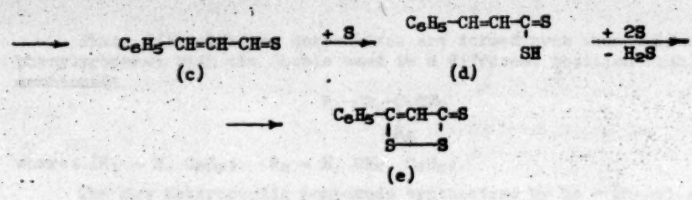
These four compounds represent all the possible mono- and diphenyldithiolthiones and one of the two possible isomers of methylphenyldithiolthione.* We were unable to synthesize either the second isomer (α-methyl-β-phenyldithiolthione) or the higher substitution products in the heterocyclic alkylphenyldithiolthiones by sulfurizing the phenol olefins. The reason for this is that the initial hydrocarbons, which might be converted into the foregoing compounds by the action of sulfur, contain four or more carbon atoms as a straight chain and are therefor converted into the corresponding phenylthiophenes [1,8-10].

The hypothetical mechanism of the reaction involving the sulfurizing of the phenylpropenes, which results in the formation of phenyl-substituted dithiolthiones, may be represented as follows (taking 1-phenylpropene-1 as our example). At the start, the reaction with sulfur is the same as in the formation of the phenylthiophenes [1], i.e., substitution takes place at the α-methyl group, with the formation of β,γ-unsaturated mercaptans (b). But in this case the S-oxidation reaction does not stop at this stage, but continues further to the thiocinnamic aldehyde (c), and, finally, to carbithiocinnamic acid (d). The latter reacts with sulfur, splitting off a molecule of hydrogen sulfide and forming the corresponding phenyldithiolthione (e):

C_6H_5–CH=CH–CH_3 $\xrightarrow{+S}$ C_6H_5–CH=CH–CH_2SH $\xrightarrow[-H_2S]{+S}$

(a) (b)

* 4-Methyl-5-phenyl-1,2-dithiol-3-thione, which served us in our discovery of the new direction taken by the reaction of sulfurizing unsaturated compounds, was investigated by us particularly thoroughly; it was also studied goniometrically and roentgenographically. [14].

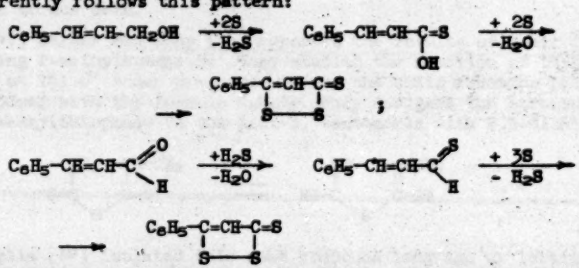


This diagram of the reaction mechanism is corroborated by the following facts. The fact that the sulfurizing of unsaturated compounds usually starts with a substitution in the alpha position of the double bond is firmly established at the present time [1]. The further formation of thioaldehyde is probable because in reacting 1-phenylpropene-1 with sulfur we isolate a compound with the composition of C_9H_8S, which apparently is a polymer of thiocinnamic aldehyde. Finally, a compound whose composition corresponded to that of carbithiocinnamic acid was isolated by Manseau [15] when sulfur was reacted with anethole as follows:

$$C_{10}H_{12}O + 3S \longrightarrow C_{10}H_{10}OS_2 + H_2S.$$

Moreover, the foregoing mechanism diagram is analogous to the above-mentioned reaction of ethyl cinnamate with sulfur, which results in the formation of α-phenyldithiolthione.

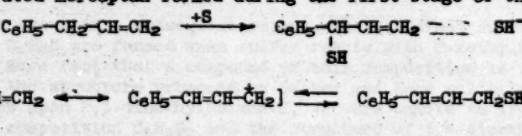
To confirm this diagram we also studied the sulfurization of cinnamic acid and aldehyde. In both cases α-phenyldithiolthione was isolated. The reaction apparently follows this pattern:



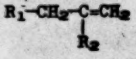
Derivatives of 1,2-dithiol-3-thione are also formed when unsaturated compounds containing an allyl group are sulfurized. Thus, we synthesized α-phenyldithiolthione by allowing sulfur to act upon allylbenzene. In this instance we had to assume either preliminary isomerization with a shift of the double bond toward the aromatic ring:

$$C_6H_5-CH_2-CH=CH_2 \longrightarrow C_6H_5-CH=CH-CH_3,$$

which usually occurs quite readily [16,17], or else an allyl rearrangement of the β,γ-unsaturated mercaptan formed during the first stage of the reaction:



Thus, dithiolthione derivatives are formed even when sulfur acts on phenylpropenes with the double bond in a different position than that previously mentioned:



where: (R_1 = H, C_6H_5; R_2 = H, CH_3, C_6H_5).

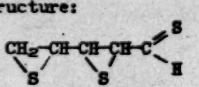
The new heterocyclic compounds synthesized by us – phenyl-substituted dithiolthiones – are beautifully crystallizing substances that are bright-orange or red in color and melt into blood-red liquids at temperatures above 100°. Their color is due to the chromophore thiocarbonyl group linked to the disulfide chain. The ready availability of these compounds makes the possibility of their use as dyestuffs an interesting problem.

The phenylated dithiolthiones are physiologically active. They have an extremely bitter taste. Their fumes (and those of some of their derivatives, especially their iodomethylates) are irritants and leave an extremely bitter taste in the mouth that persists for a long time.

After the experimental section of the present research had been completed and part of our results had been published [1,2], we had to opportunity of acquainting ourselves with the just-published research of other authors, who had been working at the same time as we had been and had also synthesized some dithiolthione derivatives, although in some cases the latter had been assigned a different structure. We did not hesitate to revise our manuscript, which had been already prepared for press, to allow for consideration of this work in the light of our data.

In 1947, Selker and Kemp [18] reported the results of their investigation of sulfurizing 2-methylbutene-2. They studied the reaction of this hydrocarbon with sulfur at 141.6° under pressure. Among the solid reaction products they found a compound with the formula $C_5H_8S_3$. They assigned the structure of 2,5-dithione-3-methylthiophane to the latter, tautomeric with 2,5-dithiol-3-methylthiophene:

Barbaglia [19] isolated this same compound long ago by letting sulfur react with isovaleraldehyde, as well as by the cited authors, Barbaglia assigning the following structure:

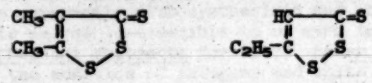


to it and pointing out that this compound is formed from thiovaleraldehyde as follows:

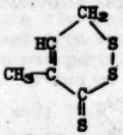
$$C_5H_{10}O \xrightarrow{+S} C_5H_{10}S \xrightarrow{+4S} C_5H_8S_3 + 2H_2S.$$

As will be shown in a subsequent report, two different substances with the composition $C_5H_8S_3$ are formed when sulfur reacts with 2-methylbutene-2 and pentene-2. The mere fact that a compound of this composition is formed from pentene-2 makes the structure proposed by Selker and Kemp unlikely. Moreover, when sulfur acted upon 2,3-dimethylbutene-2, we were unable to isolate a compound of the composition $C_5H_8S_3$ and the structure of 3,4-dimethyl-2,5-di-

thiolthiophene no matter what conditions were employed, though its formation should have been expected on the basis of the views of the American authors. On the basis of our data, the structure of dithiolthione derivatives must be assigned to the products of the sulfurization of aliphatic olefins. Thus, the compound $C_5H_6S_3$ synthesized from 2-methylbutene-2 is, contrary to what Selker and Kemp assert, 4,5-dimethyl-1,2-dithiol-3-thione, and the compound of the same composition synthesized from pentene-2 is 5-ethyl-1,2-dithiol-3-thione:

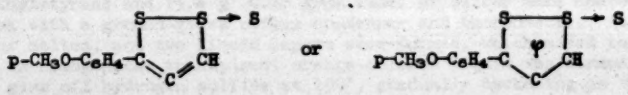


In the paper by Selker and Kemp we found a reference to the unpublished data of Bottcher and Luttringhaus [20], who worked in Germany during World War II. These authors also synthesized compounds analogous to those with the $C_5H_6S_3$ composition and called them "trithiones." One of them was synthesized with a yield of 5% when sulfur was reacted with isoprene. The above-cited structure of 4,5-dimethyl-1,2-dithiol-3-thione, i.e. the structure adopted by us:



was assigned to this compound, but this is, apparently, less probable.

In 1947, Gaudin and Pottier [21] synthesized orange crystals, with the structure of $p\text{-}CH_3O\text{-}C_6H_4\text{-}C_3HS_3$, called trithioanethole, by sulfurizing anethole ($p\text{-}CH_3O\text{-}C_6H_4\text{-}CH{=}CH\text{-}CH_3$).* The structure of the $-C_3HS_3$ remained unclear to the authors. Somewhat later, Gaudin and Lozach [22] synthesized this same compound by reacting sulfur with estragole ($p\text{-}CH_3O\text{-}C_6H_4\text{-}CH_2\text{-}CH{=}CH_2$). The following two structures (which are quite improbable from our standpoint) were suggested for trithioanethole:

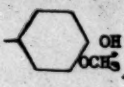


where φ = an electronic sextet.

Only in his third communication [24], devoted to the action of sulfur upon eugenol** and isoeugenol, did the French chemist (Lozach) reach the correct structure for trithioanethole and related compounds. In both instances, the reaction was similar to that described for anethole, "trithioeugenol," which was assigned the structure of a dithiolthione derivative:

* Manseau [18] and Bottscher [23] also effected the reaction of sulfur with anethole, as Gaudin and Pottier point out. The data of these authors are unavailable to us, nor are they abstracted anywhere.

** Baumann and Fromm [25] were the first to sulfurize eugenol.

(where: R = 

)

being formed. Lozach points out that, after his research had been completed, he learned of the just-published paper by Bottcher and Luttringhaus [28], who had just done research on trithioanethole and come to a similar conclusion concerning the structure of the $-C_3HS_3$ group. Unfortunately, the work done by these authors, who have apparently also synthesized and studied the derivatives of dithiolthione, is as yet inaccessible to us even in abstract form (it is not abstracted in Chemical Abstracts for 1947). Later on, Lazach and Gaudin [27] investigated the addition of halogens and salts of the heavy metals to trithioanethole.

EXPERIMENTAL

Synthesis of 4-Methyl-5-phenyl-1,2-dithiol-3-thione (β-methyl-α-phenyldithiolthione)

2-Methyl-1-phenylpropene-1 (β,β-dimethylstyrene). The initial hydrocarbon was prepared by dehydrating dimethylbenzylcarbinol in the presence of iodine. The alcohol was synthesized from benzylmagnesium chloride and acetone. The synthesized phenyl olefin was purified by distilling in vacuum over metallic sodium, followed by distillation at atmospheric pressure into a column:

B.p. 184.3° (770.8 mm); 76.2° (13.5 mm); d_4^{20} 0.8983; n_C^{20} 1.52418; n_D^{20} 1.52967; n_F^{20} 1.54471.

Parachore:

P^{20} 31.86. Found: P 349.7.

Calculated: P 352.1 (Segden method); 350.6 (by Mumford and Phillips).

Literature data for 2-methyl-1-phenylpropene-1: Auwers and Eisenlohr [29]: B.p. 183-185° (757 mm); $d_4^{19.6}$ 0.8986; $n_C^{19.6}$ 1.52185; $n_D^{19.6}$ 1.52733; $n_F^{19.6}$ 1.54105. (Cf. also [29]).

Action of sulfur on 2-methyl-1-phenylpropene-1. 31.7 g (0.24 mole) of β,β-dimethylstyrene and 15.4 g (0.48 gram atom) of sulfur were heated together in a flask with a ground-glass reflux condenser and thermometer. At about 90° the sulfur melted, and two liquid layers were formed, which mixed thoroughly at 180°. A homogeneous transparent orange-colored liquid was formed, which began to give off hydrogen sulfide at 190°, gradually darkening as this went on and becoming opaque. The reaction lasted 10 hours at 190-210°. The reaction product (38.2 g) hardened into a thick black crystalline mass upon cooling. Distillation in vacuum yielded 13.6 g of a hydrocarbon with a b.p. of 53-55° (4 mm). Another fraction was collected with a b.p. of 204-210° (1.5 mm)*. This substance was recrystallized from acetone, yielding small, shining orange crystals. They were washed several times with boiling ether and were recrystallized from alcohol, the hot alcohol solution being treated with metallic sulfur to remove any traces of free sulfur. The yield of the substance with a m.p. of 104.5-104.8° was 19.0 g, or 80% of theory, based on the reacted hydrocarbon.

The synthesized substance, which was recrystallized a few more times from acetone, consists of beautiful, transparent, lustrous, elongated, orange-red platelets with well-defined faces:

* This was a dark-red viscous liquid that solidified upon cooling.

M.p. 104.8°; b.p. 208-209° (1.5 mm); d_4^{20} 1.450.

0.2432 g substance: 22.883 g benzene: Δt 0.246°.
0.4022 g substance: 22.60 g benzene: Δt 0.410°.
Found: M 222.2, 222.7.
$C_{10}H_8S_3$. Calculated: M 224.36.

0.1030 g substance: 0.2022 g CO_2; 0.0304 g H_2O.
0.1010 g substance: 0.1981 g CO_2; 0.0328 g H_2O.
Found %: C 53.57; 53.52; H 3.30, 3.38.
$C_{10}H_8S_3$. Calculated %: C 53.53; H 3.59.

Sulfur determination (Gasparini method):

0.1222 g substance: 0.3817 g $BaSO_4$.
0.1296 g substance: 0.4056 g $BaSO_4$.
Found %: S 42.90, 42.98.
$C_{10}H_8S_3$. Calculated %: S 42.87.

In the melted state the substance synthesized is blood-red liquid, with a tendency toward supercooling. In powdered form it is bright orange in color. The substance is readily soluble in the cold in benzene, hydrogen sulfide, and acetone; it is poorly soluble in methanol, ethyl alcohol, and glacial acetic acid. When heated it is readily soluble in all the usual organic solvents. It is insoluble in boiling water or (in the cold) in concentrated hydrochloric or hydrobromic acid or in alkalies. It is not volatile with steam. Very large ruby-red lamellar crystals (up to several centimeters in size) can be obtained by means of slow crystallization from benzene. From alcohol the substance crystallizes as highly lustrous, golden-yellow lamellae, and as elongated bright-orange platelets from glacial acetic acid or hydrogen sulfide. It dissolves violently in cold concentrated nitric acid. It is readily oxidized by dilute nitric acid (sp. gr. 1.12) or perhydrol to benzoic acid (m.p. 121.0-121.2° after recrystallization from hot water; its identity proved by mixed test sample) and sulfuric acid (precipitated as $BaSO_4$). When it is boiled with an aqueous solution of NaOH or KOH the corresponding benzoate is separated out (subsequently converted into the free acid; its identity proved by a mixed test sample). It dissolves in concentrated sulfuric acid and is precipitated as a bright-orange powder when the solution is diluted with water. It yields a stable cherry-red color with sodium nitroprusside and alkali (Grothe's reagent). In benzene solution the substance does not react with metallic sodium or with zinc or copper dust, even when heated. In a hydrogen-sulfide medium an orange-yellow addition product is formed with bromine or chlorine. When a solution of mercuric bromide (or chloride) in acetone is added to a solution of the substance in the same solvent, a bright-yellow precipitate of a mercury derivative is thrown down instantaneously and, apparently, quantitatively.* The complex mercury compound is hardly soluble at all in organic solvents. When recrystallized from a large volume of boiling toluene, it consists of tiny golden-yellow crystals with a m.p. of 215.2° (with decomposition), corresponding to a formula of $C_{10}H_8S_3 \cdot HgBr_2$.

Found %: S 16.85, 16.93; Hg 34.00, 33.92.
$C_{10}H_8S_3 \cdot HgBr_2$. Calculated %: S 16.45; Hg 34.30.

The coordination compound with $HgBr_2$ is readily soluble in hot nitric acid.

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* We successfully employed this reaction with ensuing decomposition of the mercury coordination compound formed by an aqueous solution of NaOH + Na_2S to isolate the monophenyldithiolthiones in pure state when we synthesized them.

The substance also forms addition products readily with a number of other salts of heavy metals (particularly the halides). Thus, orange-colored coordination compounds were obtained with $HgCl_2$, $ZnCl_2$, ZnClI, $CdCl_2$, $AuCl_3$, $BiCl_3$, $AgNO_3$, $PtCl_4$, $PdCl_2$; a reddish-brown coordination compound with Cu_2Br_2; and a brown coordination compound with $FeCl_3$.

The substance dissolves readily in methyl iodide. A precipitate of the iodomethylate (0.1491 g from 0.0968 g of substance) – brick-orange crystals with a m.p. of 136° with decomposition, which is insoluble in the usual organic solvents, is quickly thrown down (instantaneously upon heating) from the solution.

Sulfur determination (Gasparini Method):

0.0942 g substance: 0.1317 g $BaSO_4$.
0.0813 g substance: 0.1149 g $BaSO_4$.
Found %: S 19.20.
$C_{10}H_8S_3 \cdot 2CH_3I$. Calculated %: S 18.93.

The substance is readily reduced by sodium in isoamyl alcohol, being decolored in so doing; we were unable, however, to isolate any individual products of reduction (only Na_2S was isolated); it was reduced just as easily by zinc dust in glacial acetic or formic acid, forming ZnS and a slight amount of hydrogen sulfide. Slight quantities of small, white, platelike crystals and orange-yellow liquids, which were not investigated any closer, were isolated from the reduction products.

The substance does not liberate methane from methylmagnesium iodide in an ether solution.

Thus, all the cited data * testify to the fact that the synthesized substance is 4-methyl-5-phenyl-1,2-dithiol-3-thione (β-methyl-α-phenyldithiolthione).

In our second experiment, 46.3 g (0.35 mole) of 2-methyl-1-phenylpropene-1- and 33.7 g (1.05 gram atom) of sulfur were heated for 8 hours to 200-210°. The reaction product was extracted with boiling alcohol. 46 g of pure substance was isolated as golden-orange platelets with a m.p. of 104.6-104.8° from the alcohol solution after it had been treated with metallic mercury and recrystallized from the same solvent. The yield of β-methyl-α-phenyldithiolthione was 89%, based on the sulfur taken for the reaction.

The third experiment investigated the sulfurization of 2-methyl-1-phenylpropene-1 under conditions that caused no liberation of hydrogen sulfide. Thus, 5.29 g (0.04 mole) of the phenyl olefin and 3.84 g (0.12 gram atom) of sulfur were heated in a test tube with a ground-glass reflux condenser. A thermometer was immersed into the reaction mixture. Absolutely no hydrogen sulfide was liberated during 20 hours of heating at 165-170°. The reaction product, which was a homogeneous, transparent, viscous, dark-brown liquid, was dissolved in acetone and treated with metallic mercury to remove any traces of free sulfur. When the orange-red solution was treated with an acetone solution of $HgBr_2$, a copious, characteristic, yellow precipitate of the mercury derivative of β-methyl-α-phenyldithiolthione settled out at once. Absolutely pure β-methyl-α-phenyldithiolthione, with a m.p. of 104.8°, was isolated from the latter after treatment with an aqueous solution of NaOH and Na_2S, followed by recrystallization. This experiment proves that the hydrogen sulfide formed during the reaction is completely absorbed in the secondary reactions.

Cf [14] for data on the goniometric and X-ray analysis of the β-methyl-α-phenyldithiolthione synthesized by us.

* The other phenyl-substituted dithiolthiones described below possess chemical properties that resemble those cited above, and we shall therefore not dwell on them in such detail.

Synthesis of 4,5-Diphenyl-1,2-dithiol-3-thione (α,β-Diphenyldithiolthione)

1,2-Diphenylpropene-1 (α-methylstilbene). The initial 1,2-diphenylpropene-1 was synthesized by dehydrating methylphenylbenzylcarbinol in the presence of iodine. This aromatic alcohol, in turn, was prepared from benzylmagnesium chloride and acetophenone. The hydrocarbon, synthesized with a yield of 56% of the theoretical, was refined by vacuum distillation followed by recrystallization from alcohol; after which its constants were:

M.p. 82.0-82.5°; b.p. 285.0° (756 mm); 163.2° (12 mm); 154.7° (7 mm).

Literature data for 1,2-diphenylpropene-1: Klages [30]: M.p. 82-83°; b.p. 285-286°; 183° (26 mm); d_4^{17} 0.9857; n_D^{17} 1.5635. Auwers and Kraul [31]: M.p. 82-83°; b.p. 165° (13 mm); $d_4^{99.9}$ 0.9565; $n_C^{99.9}$ 1.58352; $n_D^{99.9}$ 1.59180; $n_F^{99.9}$ 1.61469.

Action of sulfur on 1,2-diphenylpropene-1. 19.3 g (0.1 mole) of the hydrocarbon and 12.8 g (0.4 gram atom) of sulfur were heated in a small flask, fitted with a reflux air-cooled condenser and a thermometer. Above 130° all the sulfur entered solution, coloring it pale yellow. At 180° this turned to orange, then to red, and finally, to a beautiful dark-red. Only at 190° did the liberation of hydrogen sulfide become noticeable. The reaction mixture was heated for 24 hours at 180°. After this heating it was a dark-red liquid, transparent only in a thin layer and hardening to a red crystalline mass upon cooling. The crystals were dissolved in ligroin (b.p. 100-150°) and, after the free sulfur had been eliminated by treatment with metallic mercury, they were recrystallized several times from the same solvent. The yield of the substance was 18.2 g, or 80% of the theoretical, based on the sulfur initially employed.

The substance synthesized consists of small, carmine-red acicular crystals, possessing a high luster. M.p. 160.4-160.5°.

0.2376 g substance: 16.90 g benzene: Δt 0.255°.
0.2510 g substance: 17.05 g benzene: Δt 0.270°.
Found: M 282.8, 279.7.
$C_{15}H_{10}S_3$. Calculated: M 286.53.

0.1007 g substance: 0.2321 g CO_2; 0.0326 g H_2O.
0.1018 g substance: 0.2334 g CO_2; 0.0322 g H_2O.
Found %: C 62.93, 62.57; H 3.62, 3.54.
$C_{15}H_{10}S_3$. Calculated %: C 62.90; H 3.52.

Sulfur determination (Gasparini Method):

0.1214 g substance: 0.2956 g $BaSO_4$.
0.1197 g substance: 0.2917 g $BaSO_4$.
Found %: S 33.44, 33.47.
$C_{15}H_{10}S_3$. Calculated %: S 33.58.

α-β-Diphenyldithiolthione is readily soluble in ether, hydrogen sulfide, and acetone, and hot alcohol, benzene, and ligroin; it dissolves with difficulty in the cold in benzene, ligroin, and petroleum ether. It is easily soluble in concentrated nitric and sulfuric acids. It is insoluble in boiling water, hydrochloric acid, and alkalies. It crystallizes from acetone or alcohol as bright-red silky needles. With bromine it forms a lemon-yellow addition product. With methyl iodide it easily forms a red crystalline precipitate of the iodomethylate, even in the cold, which corresponds to a compound of the formula $C_{15}H_{10}S_3 \cdot 2CH_3I$, with a m.p. of 170-171.5° (after repeated washing with boiling benzene) that is insoluble in ordinary organic solvents.

Sulfur determination (Gasparini Method):

0.0854 g substance: 0.1030 g $BaSO_4$.
0.0995 g substance: 0.1184 g $BaSO_4$.
Found %: S 16.56, 16.34.
$C_{17}H_{16}S_3I_2$. Calculated %: S 16.86.

α,β-Diphenyldithiolthione is readily oxidized by dilute nitric acid or perhydrol into benzoic acid. The latter is also formed when the substance is cleaved by boiling it with an alkali. It yields no precipitate with an acetone solution of mercuric bromide (the mercury derivative is soluble in acetone). It yields a stable cherry-red color with sodium nitroprusside and alkali.

Synthesis of 4-Phenyl-1,2-dithiol-3-thione (β-Phenyldithiolthione)

2-Phenylpropene-1 (α-methylstyrene). The initial phenyl olefin was synthesized by dehydrating dimethylphenylcarbinol in the presence of iodine. The alcohol was synthesized from methylmagnesium iodide and acetophenone or from phenylmagnesium bromide and acetone. In each case, the synthesized hydrocarbon was distilled twice at atmospheric pressure and once in vacuum:

B.p. 163.5° (763.1 mm); 60.0° (17 mm); d_4^{20} 0.9082; n_C^{20} 1.52778; n_D^{20} 1.53344; n_F^{20} 1.54813.

Parachor:

P^{20} 31.99. Found: P 309.5.
Calculated: P 309.1 (Segden); 310.6 (Memford and Phillips).

Literature data for 2-phenylpropene-1: Auwers and Eisenlohr [28]: B.p. 162-165°; 54.5-55° (14 mm); $d_4^{19.8}$ 0.9078; $n_C^{19.8}$ 1.52893; $n_D^{19.8}$ 1.53492; $n_F^{19.8}$ 1.54959. Cf. also [29].

Action of sulfur on 2-phenylpropene-1. 28.0 g (0.23 mole) of the initial phenyl olefin and 29.5 g (0.92 gram atom) of sulfur were heated for 12 hours to 200-215° until no more hydrogen sulfide was evolved. The reaction product, a black tarry mass, was extracted with boiling methanol. After the alcohol solution had been treated with metallic mercury, it yielded 11.1 g of orange crystals, which were recrystallized several times from ethyl alcohol. The yield of pure substance – beautiful elongated, orange-colored, acicular crystals with a m.p. of 122.8° – was 9.2 g, or 42% of the theoretical, based on the sulfur initially employed.

0.0806 g substance: 11.53 g benzene: Δt 0.170°.
0.0884 g substance: 11.32 g benzene: Δt 0.189°.
Found: M 210.9, 211.0.
$C_9H_6S_3$. Calculated: M 210.34.

Sulfur Determination (Gasparini Method).

0.1230 g substance: 0.4107 g $BaSO_4$.
0.1198 g substance: 0.4005 g $BaSO_4$.
Found %: S 45.86, 45.92
$C_9H_6S_3$. Calculated %: S 45.73.

The substance is soluble in the ordinary organic solvents. It forms benzoic acid when oxidized by dilute nitric acid. It instantaneously forms the characteristic precipitate of the mercury derivative, with a melting point of about 170° with strong decomposition, when treated with an acetone solution of mercuric bromide. When treated with methyl iodide, it rapidly forms a precipitate of the iodomethylate, even in the cold, as orange-red crystals that are

insoluble in ordinary organic solvents.

Sulfur Determination (Gasparini Method):

0.1007 g substance: 0.1451 g $BaSO_4$.
0.0743 g substance: 0.1080 g $BaSO_4$.
Found %: S 19.69, 19.96.
$C_9H_8S_3 \cdot 2CH_3I$. Calculated %: S 19.46.

When an alcoholic solution of the substance is boiled with hydroxylamine hydrochloride and sodium acetate, precipitation with water yields an oxime with the composition of $C_9H_7ONS_2$ as small yellow crystals with a m.p. of 172.5° with decomposition.

0.0801 g substance: 4.75 ml N_2 (18°, 751 mm).
0.0763 g substance: 4.53 ml N_2 (18°, 751 mm).
Found %: N 6.73, 6.74.
$C_9H_7ONS_2$. Calculated %: N 6.69.

Synthesis of 5-Phenyl-1,2-dithiol-3-thione (α-Phenyldithiolthione)

1-Phenylpropene-1 (β-methylstyrene). The initial hydrocarbon was prepared by dehydrating phenylethylcarbinol with phosphoric acid. The alcohol was synthesized from methylmagnesium bromide and benzaldehyde. The synthesized hydrocarbon was distilled twice with a column:

B.p. 176.2° (754 mm), 66.0° (11 mm); d_4^{20} 0.9139; n_C^{20} 1.5424; n_D^{20} 1.5491; n_F^{20} 1.5659.

Parachor:

γ^{20} 34.12. Found: P 312.5.
Calculated: P 313.1 (Segden); 313.6 (Memford and Phillips).

Literature data on 1-phenylpropene-1: Auwers and Eisenlohr [28]: B.p. 65.5°(11 mm); $d_4^{18.7}$ 0.9145; $n_C^{18.7}$ 1.54257; $n_D^{18.7}$ 1.54967; $n_F^{18.7}$ 1.5660; Levina [18] B.p. 171-173°; d_4^{20} 0.9130; n_D^{20} 1.5400: Klages [32]: B.p. 177° (756 mm), 74° (13 mm); d_4^{20} 0.9; n_D^{20} 1.5492.

Action of sulfur on 1-phenylpropene-1. 11.8 g (0.1 mole) of β-methylstyrene and 9.6 g (0.3 gram atom) of sulfur were placed in a small round-bottomed flask fitted with a reflux condenser and a thermometer. The reaction mixture was heated to 190°. Two layers formed: the lower one containing sulfur; and the upper one containing its solution in the hydrocarbon, yellow in color, which turned orange and then red as heating continued. After 3 hours of heating, all the sulfur entered solution; the reaction mixture became homogeneous and had a dark color (brownish-orange in a thin layer). The reaction was continued for 25 hours at 190°. Only a slight amount of hydrogen sulfide was evolved in the reaction. The reaction product, a black pitchlike mass, was extracted with boiling alcohol. What was left behind was a black tar, most of which dissolved in benzene. 3.8 g of pure substance with a m.p. of 126.2° * (after double recrystallization from alcohol), as lustrous orange platelets, was isolated from the alcoholic extract after the latter had been treated with metallic mercury. The yield of α-phenyldithiolthione was 30%, based on the sulfur initially employed.

0.1236 g substance: 16.75 g benzene: Δt 0.177°.
0.2534 g substance: 16.75 g benzene: Δt 0.361°.
Found: M 214.2, 215.0.
$C_9H_8S_3$. Calculated: M 210.34.

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* A typographical error in the preliminary report [2] cited the melting point of α-phenyldithiolthione erroneously (123.2° instead of 126.2°).

Sulfur Determination (Gasparini method):

0.1003 g substance: 0.3323 g $BaSO_4$.
0.0965 g substance: 0.3200 g $BaSO_4$.
Found %: S 45.50, 45.55.
$C_9H_6S_3$. Calculated %: S 45.73.

The substance crystallizes from acetone as lustrous, long, thin dark-orange needles. It is completely oxidized to benzoic acid when oxidized with 20% nitric acid at 90-95° in a sealed tube. The former acid is also formed when the substance is oxidized by perhydrol or cleaved by alkalies. When treated with an acetone solution of mercuric bromide, it instantaneously forms the characteristic bright-yellow precipitate of the mercury derivative, with a m.p. of 155°. With methyl iodide it readily forms a precipitate of the iodomethylate as small, bright-orange crystals that dissolve with difficulty in ordinary organic solvents (0.1259 g of substance yielded 0.1680 g of the iodomethylate). After several washings with boiling benzene, the iodomethylate had a m.p. of 155°.

Sulfur Determination (Gasparini Method):

0.1113 g substance: 0.1611 g $BaSO_4$.
0.0615 g substance: 0.0879 g $BaSO_4$.
Found %: S 19.88, 19.63.
$C_9H_6S_3 \cdot 2CH_3I$. Calculated %: S 20.02.

When the iodomethylate is boiled with a solution of $AgNO_3$, no AgI precipitate is formed.

In an acetone solution at room temperature α-phenyldithiolthione is very easily oxidized by permanganate (when the components are mixed, a copious precipitate of MnO_2 is thrown down at once). The oxidation reaction was effected with the calculated quantity of $KMnO_4$ (3.2 g per 2.0 g of substance) with agitation for one hour. The precipitate of manganese dioxide was filtered out and washed with acetone. Light-red crystals with a singular, fairly pleasant odor were isolated from the solution. They had a m.p. of 116.6-117° after double recrystallization from alcohol.

0.0391 g substance: 12.43 g benzene: Δt 0.083°.
0.0372 g substance: 12.42 g benzene: Δt 0.079°.
Found: M 194.4, 194.3.
$C_9H_6S_2O$. Calculated: M 194.27.

Sulfur Determination (Gasparini Method)

0.0562 g substance: 0.1371 g $BaSO_4$.
0.0498 g substance: 0.1208 g $BaSO_4$.
Found %: S 33.50, 33.33.
$C_9H_6S_2O$. Calculated %: S 33.01.

When an alcoholic solution of the substance is boiled with hydroxylamine hydrochloride in the presence of sodium acetate, H_2S is evolved and the oxime is formed, consisting of golden-yellow needles with a m.p. of 137-139° (after recrystallization from benzene).

0.0811 g substance: 4.83 ml N_2 (21°, 760 mm).
0.0837 g substance: 4.95 ml N_2 (21.5°, 756 mm).
Found %: N 6.70, 6.73.
$C_9H_7ONS_2$. Calculated %: N 6.69.

Allylbenzene (1-phenylpropene-2). Allylbenzene was synthesized from

phenylmagnesium bromide and allyl bromide, by Hekshlevy's method [33]. The synthesized hydrocarbon was treated for a long time in the cold with metallic sodium and, after the latter had been eliminated, double distilled with a column:

B.p. 158.6° (767 mm); d_4^{20} 0.8920; n_C^{20} 1.50634; n_D^{20} 1.51103; n_F^{20} 1.52287.

Parachor:

P^{20} 30.37. Found: P 311.5.
Calculated: P 313.1 (Segden); 313.6 (Mumford and Phillips).

Literature data on allylbenzene. Levina [18]: B.p. 156-157° (751 mm); d_4^{20} 0.8923; n_D^{20} 1.5131; MacKenna and Sowa [34]: B.p. 156-159°; d_4^{25} 0.8812; n_D^{25} 1.5042.

Action of sulfur on allylbenzene. 65.5 g (0.55 mole) of allylbenzene and 53.0 g (1.65 gram atoms) of sulfur were heated in a round-bottomed flask with a reflux condenser and a thermometer. At 170°, the reaction mixture became homogeneous and turned bright red, darkening as heating continued. The reaction was effected for 8 hours at 200-210°. The reaction product was extracted with boiling ethyl alcohol. The alcoholic solution was treated with metallic mercury, after which 10.5 g of absolutely pure α-phenyldithioldithione with a m.p. of 126.2-126.4° was isolated from it; its identity was established by a mixed test sample. A mixed test sample with β-phenyldithioldithione exhibited a marked depression (fused at 119°). The tar remaining behind after extraction was dissolved in ligroin (b.p. 200-220°). The crystals that settled out of the solution were recrystallized several times from the same solvent.

The pure substance,* the yield of which increases as the reaction temperature is raised, consists of small, yellowish, lamellar crystals, with a m.p. of 324.3-324.8°, which are insoluble in ordinary organic solvents and dissolve with difficulty in camphor. This latter circumstance made it impossible to determine the molecular weight of the synthesized substance. Combustion data indicate that its composition is that of thiocinnamic aldehyde, C_9H_8S.

0.0642 g substance: 0.1712 g CO_2; 0.0312 g H_2O; 0.1033 g $BaSO_4$.
0.0922 g substance: 0.2469 g CO_2; 0.0440 g H_2O; 0.1382 g $BaSO_4$.
Found %: C 72.77, 73.09; H 5.44, 5.34; S 22.07, 20.59.
C_9H_8S. Calculated %: C 72.92; H 5.44; S 21.63.

The substance is oxidized with difficulty by nitric acid; for that reason sulfur was not determined by the Gasparini method, but while the substance was burned to carbon and hydrogen in the presence of manganese dioxide.

Action of Sulfur Upon Cinnamic Alcohol

69.9 g (0.52 mole) of cinnamic alcohol and 66.8 g (2.1 g atoms) of sulfur were heated together for 15 hours at 200-215° until no more hydrogen sulfide was evolved. At first the reaction was violent and accompanied by the liberation of water. The reaction mixture was extracted with methanol. After the alcoholic solution had been treated with mercury, 5.3 g of pure α-phenyldithioldithione, with a m.p. of 126.0°, was isolated. A test sample gave no depression when mixed with standard pure α-phenyldithioldithione. A slight amount of small white crystals soluble in benzene was also isolated; they were not subjected to further analysis.

Action of Sulfur on Cinnamic Aldehyde

51.9 g (0.4 mole) of cinnamic aldehyde, freshly distilled in vacuum, and 38.0 g (1.2 gram-atoms) of sulfur were heated at 200-220° for 20 hours. The

* This same substance was isolated when sulfur was reacted with β-methylstyrene.

reaction was accompanied by the evolution of water (2.6 g) and of hydrogen sulfide. The reaction product, which was a thick black mass, was extracted with alcohol. When the alcoholic solution was treated with methyl iodide, small golden-yellow crystals of 5-phenyl-1,2-dithiol-3-thione iodomethylate, with a m.p. of 154° (after repeated washing with boiling benzene), precipitated out. A test sample mixed with the 5-phenyl-1,2-dithiol-3-thione iodomethylate previously prepared caused no noticeable depression.

Sulfur Determination (Gasparini Method)

0.0841 g substance: 0.1208 g $BaSO_4$.
0.0783 g substance: 0.1140 g $BaSO_4$.
Found %: S 19.72, 20.00.
$C_9H_6S_3 \cdot 2CH_3I$. Calculated %: S 19.46.

SUMMARY

1. The reaction of sulfur with α-methylstyrene, β-methylstyrene, β,β-dimethylstyrene, α-methylstilbene, allylbenzene, cinnamic alcohol, and cinnamic aldehyde has been investigated.

2. It has been shown that when sulfur acts upon phenol olefins with $R_1-CH=C(R)CH_3$ or $R_1-CH_2-C(R_2)=CH_2$ (R_1 = H, C_6H_5; R_2 = H, CH_3, C_6H_5) structures, phenyl-substituted 1,2-dithiol-3-thiones:

are smoothly formed.

3. All the possible mono- and diphenyl-1,2-dithiol-3-thiones and 4-methyl-5-phenyl-1,2-dithiol-thione have been synthesized.

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THE REACTION OF AROMATIC SULFO ACIDS WITH PHENOLS

N. N. Vorozhtsov* and A. B. Kuchkarov

Dyestuffs Laboratory of the Mendeleyev Institute of Chemical Technology, Moscow

The aromatic sulfones have been known for a long time as side products formed during the sulfonation of various hydrocarbons, but up to the present time the reason for their formation in the sulfur mass is still not entirely clear. Similarly, comparatively little light has been shed upon the individual members of this group of chemical compounds in the literature, in spite of the fact that some of these compounds are beginning to find practical application in the synthesis of complex azo dyes, tanning agents, and synthetic resins [1].]

Particularly little research has been done on the hydroxy diaryl sulfones. Most of the published research in this field has been devoted chiefly to problems of the isolation of the hydroxy sulfones from the products synthesized by the action of sulfuric acid upon aromatic phenols: Glutz [2], for instance, was the first to effect the synthesis of 4,4-dihydroxydiphenylsulfone by heating phenol and sulfuric acid (to 160°).

Later, J. Zchenter [3] and his associates used Glutz's method to synthesize a number of hydroxy diaryl sulfones. Various hypotheses have been advanced concerning the nature of the chemical reaction involved in the formation of hydroxy sulfones. According to J. Zchenter, hydroxy sulfones are formed from two molecules of the sulfo acid with the liberation of a molecule of sulfuric acid or from a molecule each of the sulfo acid and phenol with the liberation of water:

$$C_6H_5OH + HOSO_2OH \longrightarrow HOC_6H_4SO_2OH + H_2O. \quad (1)$$

$$HOC_6H_4SO_2OH + HOSO_2C_6H_4OH \longrightarrow HOC_6H_4SO_2C_6H_4OH + H_2SO_4 \quad (2)$$

$$HOC_6H_4SO_2OH + HC_6H_4OH \longrightarrow HOC_6H_4SO_2C_6H_4OH + H_2O. \quad (3)$$

Research on the nature of the chemical reaction involved in the formation of sulfones is of exceptional theoretical interest in the cases of Equations (2) and (3), inasmuch as sulfone syntheses effected in accordance with these equations are closest to the reaction conditions of sulfonation during which undesirable side products – the sulfones – are usually formed.

Besides the above-mentioned equations (2) and (3), the formation of hydroxy sulfones by the action of sulfuric acid on the phenols is probably also the result of rearrangements of the phenyl esters of aromatic sulfo acids produced during the reaction, under the action of the sulfuric or sulfo acid:

(4)

The possibility of forming hydroxy sulfones in accordance with Equation (4) is corroborated by the well-known rearrangement of the phenyl esters of aromatic sulfo acids into hydroxy aryl sulfones in the presence of $AlCl_3$ or $ZnCl_2$ [4]. The results of our experiments with phenyl benzenesulfonate also speaks in favor of this course of the reaction. Thus, heating phenyl benzenesulfonate in the presence of a small quantity of sulfuric acid resulted in the the formation of 4-hydroxy diphenyl sulfone. This manner of forming the hydroxy aryl sulfones is hardly the principle factor in our experiments, however, as the rate of conversion is low. To judge by the results of our experiments, the formation of hydroxy aryl sulfones during sulfonation occurs chiefly in accordance with Equation (3). The course of the reaction of Equation (3) may be compared to the similar method of formation of hydroxy ketones from carboxylic acids and phenols in the presence of $ZnCl_2$ [5]. In the formation of hydroxy sulfones from sulfo acids and phenols, sulfuric acid possibly acts as the dehydrating agent. We first examined the possibility of sulfone formation in the sulfonation of hydrocarbons from two molecules of aromatic sulfo acids with the evolution of H_2SO_4, in accordance with Equation (2) [6]. Obtaining confirmation of the fact that the reaction follows Equation (2), we then tested the reaction of aromatic sulfo acids with phenols. The joint heating of α- or β-naphthalenesulfonic acid with phenol (200°) always yielded the same product which turned out to be 4,4'-dihydroxy-diphenyl sulfone. The formation of a sulfone that has no naphthalene group evidently is the result of the interaction of phenol and the sulfuric acid that is formed by the hydrolysis of the naphthalenesulfonic acid by the action of the reaction water that is liberated. In our subsequent tests we used the more stable benzene- and p-chlorobenzenesulfonic acids. 4-Hydroxy phenyl sulfone was synthesized by heating benzenesulfonic acid and phenol together (230-240°).

Corresponding hydroxy sulfones were synthesized by the same method, starting with ortho, para, and meta cresols and benzenesulfonic acid. o-Cresol and benzenesulfonic acid yielded 4-hydroxy-5-methyl diphenyl sulfone (yield: 43%). p-Cresol and benzenesulfonic acid yielded 4-hydroxy-6-methyl diphenyl sulfone (yield: 27%). Heating p-chlorobenzenesulfonic acid with phenol (240°) resulted in the formation of 4-hydroxy-4'-chlorodiphenyl sulfone. Similarly, 4-hydroxy-5-methyl-5'-chlorodiphenyl sulfone (33% yield) was synthesized from p-chlorobenzenesulfonic acid and o-cresol.

We also investigated the reactions yielding hydroxy diphenyl sulfones, which are characterized by a much higher reactivity than the aromatic diaryl sulfones. We synthesized the nitro-, bromo-, and acetyl derivatives of the hydroxy sulfones. The behavior of HNO_2 toward the hydroxy sulfones is of exceptional interest; it was found that no nitroso compounds are formed when molar proportions of HNO_2 are used in the usual nitrosation conditions.

The action of a considerable excess of HNO_2 on a number of sulfones results in the formation of nitro derivatives. This sort of behavior of the hydroxy diaryl sulfones when acted upon by HNO_2 was also noted by V.V.Kozlov in the case of β-hydroxy dianthrene disulfone.

EXPERIMENTAL

I. Synthesis of Hydroxy Diaryl Sulfones.

The reactions were carried out in a 100-ml three-necked flask fitted with a liquid seal, a stirrer, and a reflux condenser, which was heated over a bath of Wood's alloy. The reaction usually took 10-12 hours. The reaction mass was subjected to suitable treatment, depending on the nature of the substances synthesized, to isolate the reaction product.

1. Synthesis of 4-Hydroxy Diphenyl Sulfone

We used 9.4 g (0.1 mole) of C_6H_5OH and 7.9 g (0.05 mole) of $C_6H_5SO_3H$. The reagent mixture was heated to 230-240° for 12 hours. After the reaction was complete, the excess phenol was driven off with steam. After the residue in the distilling flask had been clarified with activated charcoal and filtered, the reaction product was obtained upon cooling as prismatic white needles. The yield was 3.90 g (37% of theory).

4-Hydroxy diphenyl sulfone [7] – crystals (from benzene), m.p. 135-136°.

0.1302 g substance: 0.2949 g CO_2; 0.0512 g H_2O.
Found %: C 61.77; H 4.36.
$C_{12}H_{10}SO_3$. Calculated %: C 61.52; H 4.27.

0.1200 g substance: 0.118 g $BaSO_4$.
Found %: S 13.47.
$C_{12}H_{10}SO_3$. Calculated %: S 13.67.

Dibromo derivative. White lamellae (from alcohol), m.p. 231-232°; synthesized by the action of 3.20 g of bromine and 2.34 g (0.01 mole) of 4-hydroxy diphenyl sulfone dissolved in 15 ml of glacial acetic acid for one hour at 18°. The mass was then diluted with cold water, and the precipitate that settled out was filtered out, dried, and recrystallized. The yield was 2.3 g (58.5% of theory).

0.2100 g substance: 10.51 ml 0.1N $AgNO_3$.
Found %: Br 39.76.
$C_{12}H_8Br_2SO_3$. Calculated %: Br 40.07.

0.1072 g substance: 0.0610 g $BaSO_4$.
Found %: S 7.82.
$C_{12}H_8Br_2SO_3$. Calculated %: S 8.16.

Mononitro derivative. Yellow lamellae (from alcohol), m.p. 131-132°; synthesized by the gradual addition of 4.5 g of nitrating mixture (in the cold) to a solution of 2.34 g of 4-hydroxy diphenyl sulfone in 10-15 ml of glacial acetic acid, with vigorous stirring. The precipitate that settled when water was added to the reaction mass was filtered out, washed, dried, and repeatedly recrystallized from methanol. The yield was 2 g (71.5% of theory).

The action of strong HNO_3 (sp. gr. 1.52) to a solution of 4-hydroxy diphenyl sulfone in glacial acetic acid at 20° likewise results in formation of the mononitro product. The yield is 75%.

5.936 mg substance: 0.273 ml N_2 (21°, 749 mm).
Found %: N 5.26.
$C_{12}H_9NSO_5$. Calculated %: N 5.01.

o-methyl derivative (4-methoxy diphenyl sulfone). Crystals (from alcohol), m.p. 90°; synthesized by heating (80-90°) an alkaline solution of 1.2 g of 4-hydroxy diphenyl sulfone with 1 g of dimethyl sulfate for 30 minutes. After the reaction is complete, the mass was cooled to room temperature and dissolved in a small quantity of cold water. The product that was thus precipitated was filtered out, dried, and recrystallized.

Acetyl derivative (4-acetoxy diphenyl sulfone). Crystals (from alcohol), m.p. 95°.

To synthesize it, 2.34 g of the hydroxy sulfone was treated in an Erlenmeyer flask with 10 g of acetic anhydride, the reaction mixture being gently heated for 20-30 minutes. Upon cooling, the reaction mass was poured into 50-75 ml of cold water, the reaction product settling out as thin prismatic needles. The yield was 2.3 g (82.0% of theory).

4.028 g substance: 8.95 mg CO_2; 1.667 mg H_2O.
Found %: C 60.59; H 4.59.
$C_{14}H_{12}SO_4$. Calculated %: C 60.86; H 4.33.

0.0684 g substance: 0.0565 g $BaSO_4$.
Found %: S 11.32.
$C_{14}H_{12}SO_4$. Calculated %: S 11.59.

2. Synthesis of 2-Hydroxy-5-methyl Diphenyl Sulfone

We used 10.8 g (0.10 mole) of p-cresol and 7.9 g (0.05 mole) of $C_6H_5SO_3H$.

The mixture was heated to 220-230° for 12 hours. After the reaction was over, the unreacted p-cresol was driven off with steam. The solid mass left in the flask was filtered out, washed, and dissolved in ethyl alcohol. The dark-red alcoholic solution produced was clarified with activated charcoal and then evaporated over a water bath to half its volume and cooled. The precipitate that settled upon cooling was filtered out, dried, and recrystallized from alcohol several times. The yield was 2.5 g (20% of theory).

2-Hydroxy-5-methyl diphenyl sulfone.[4] Rhombic crystals (from alcohol), m.p. 137-138°.

3.807 mg substance: 8.738 mg CO_2; 1.600 mg H_2O.
Found %: C 62.60; H 4.67.
$C_{13}H_{12}SO_3$. Calculated %: C 62.90; H 4.83.

0.1510 g substance: 0.140 g $BaSO_4$.
Found %: S 12.62.
$C_{13}H_{12}SO_3$. Calculated %: S 12.90.

3. Synthesis of 4-Hydroxy-5-methyl Diphenyl Sulfone

We used 32.4 g (0.3 mole) of o-cresol and 23.7 g (0.15 mole) of benzenesulfonic acid.

Heating lasted 10-12 hours at 230-240°. After the reaction was complete, the reaction mass was poured into 100-150 ml of hot water, and then the excess o-cresol was driven off with steam.

The reaction product left in the distilling flask after filtration was dissolved in 150 ml of ethyl alcohol, treated with a small amount of activated charcoal, and again filtered while still hot through Buchner funnel. The solution thus produced was evaporated over a water bath to 2/3 of its original volume and then slowly cooled. The precipitate that settled was filtered out and dried at 100°. Double recrystallization from alcohol yielded a fairly pure product as small prismatic needles. The yield was 14.8 g (43.5% of theory).

4-Hydroxy-5-methyl Diphenyl Sulfone. Crystals (from alcohol), m.p. 230-231°. It dissolves readily in methanol and ethyl alcohol, alkalies, and acids, but is poorly soluble in benzene, toluene, and ether.

5.702 mg substance: 13.102 mg CO_2; 2.418 mg H_2O.
Found %: C 62.65; H 4.75.
$C_{13}H_{12}SO_3$. Calculated %: C 62.90; H 4.93.

0.1532 g substance: 0.1440 g $BaSO_4$.
Found %: S 12.91.
$C_{13}H_{12}SO_3$. Calculated %: S 12.90.

o-Methyl derivative (4-methoxy-5-methyl diphenyl sulfone). Thin prismatic needles (from alcohol), m.p. 101-102°; synthesized by boiling a mixture of 2.48 g of the hydroxy sulfone in 25 ml of 0.5N NaOH and 2 g of dimethyl sulfate in an Erlenmeyer flask (over a water bath) for 30 minutes. The yield was 1.70 g (65% of theory).

3.203 mg substance: 7.495 mg CO_2; 1.541 mg H_2O.
Found %: C 63.82; H 5.38.
$C_{14}H_{14}SO_3$. Calculated %: C 64.12; H 5.34.

0.0256 g substance: 0.0235 g $BaSO_4$.
Found %: S 12.59.
$C_{14}H_{14}SO_3$. Calculated %: S 12.21.

Acetyl derivative (4-acetoxy-5-methyl diphenyl sulfone). Prismatic crystals (from alcohol), m.p. 98°; synthesized from 2.48 g of the hydroxy sulfone and 10 ml of acetic anhydride in the presence of a small quantity of concentrated H_2SO_4 while gently heating the mixture over a water bath for 30 minutes. Yield: 2.80 g (96% of theory).

4.721 mg substance: 10.771 mg CO_2; 2.040 mg H_2O.
Found %: C 62.22; H 4.84.
$C_{15}H_{14}SO_4$. Calculated %: C 62.06; H 4.82.
0.1004 g substance: 0.082 g $BaSO_4$.
Found %: S 11.21. $C_{15}H_{14}SO_4$. Calculated %: S 11.03.

Nitro derivative. Yellow crystals, (from alcohol), M.p. 140°.
5.675 mg substance: 0.242 ml N_2 (20°, 741 mm).
Found %: N 4.96.
$C_{13}H_{11}SNO_5$. Calculated %: N 4.77.

Bromo derivative. White crystals (from alcohol), m.p. 220°.

0.120 g substance: 3.72 ml 0.1N $AgNO_3$.
Found %: Br 24.77.
$C_{13}H_{11}SO_3Br$. Calculated %: Br 24.43.

0.1037 g substance: 0.072 g $BaSO_4$.
Found %: S 9.53.
$C_{13}H_{11}SO_3Br$. Calculated %: S 9.78.

4. Synthesis of 4-Hydroxy-6-methyl Diphenyl Sulfone

We took 21.6 g (0.22 mole) of m-cresol and 15.8 g (0.1 mole) of benzenesulfonic acid.

Heating lasted 12 hours at 220-230°. After the reaction was complete, the excess m-cresol was driven off with steam. The residue in the distilling flask was dissolved in ethyl alcohol; the alcoholic solution was clarified with activated charcoal and fractionated. At first, some m-cresol was driven over, and then, at 280-285° (6 mm) a sirupy oil, which quickly congealed into crystals. Repeated recrystallization from alcohol yielded a pure product as white lamellae that melted at 120°. Yield: 6 g (27% of theory). It is readily soluble in alcohols and nitrobenzene, but dissolves with more difficulty in benzene,

ether and toluene. It is readily soluble in caustic alkalies. It gives a red color with $FeCl_3$.

3.510 mg substance: 8.083 mg CO_2; 1.564 mg H_2O.
Found %: C 62.8; H 4.99.
$C_{13}H_{12}SO_3$. Calculated %: C 62.90; H 4.83.

0.0704 g substance: 0.0650 g $BaSO_4$.
Found %: S 12.68.
$C_{13}H_{12}SO_3$. Calculated %: S 12.90.

Dibromo derivative. Crystals, m.p. 175°; synthesized by treating a solution of 2.48 g of 4-hydroxy-6-methyl diphenyl sulfone in acetic acid with 3.5 g of bromine for 2 hours at 18°. Yield: 2.8 g (69% of theory).

The synthesized substance contains bromine and sulfur. It is readily soluble in alcohols and nitrobenzene, but dissolves less easily in benzene, toluene, and ether. It is also soluble in alkalies and acids.

0.1170 g substance: 5.73 ml 0.1 N $AgNO_3$.
Found %: Br 39.15.
$C_{13}H_{10}Br_2SO_3$. Calculated %: Br 39.38.

0.1072 g substance: 0.060 g $BaSO_4$.
Found %: S 7.69.
$C_{13}H_{10}Br_2SO_3$. Calculated %: S 7.88.

Dinitro derivative. Yellow crystals (from alcohol), m.p. 172-173°. It is synthesized by the action of 1.8 g of HNO_3 (sp. gr. 1.44) upon a solution of 2.48 g of 4-hydroxy-6-methyl diphenyl sulfone in glacial acetic acid for 1.5 to 2 hours at 18°. The yield was 2.30 g (78.0% of theory).

3.704 mg substance: 0.257 ml N_2 (19°, 745.6 mm).
Found %: N 7.96.
$C_{13}H_{10}N_2SO_7$. Calculated %: N 8.28.

Acetyl derivative, (4-acetoxy-6-methyl diphenyl sulfone). Crystals, m.p. 137-138°; synthesized by boiling a mixture of 2.48 g of 4-hydroxy-6-methyl diphenyl sulfone and 15 g of acetic anhydride in the presence of a small amount of concentrated H_2SO_4 for 30-40 minutes over a water bath. Yield: 2.70 g (95% of theory).

3.72 mg substance: 8.420 mg CO_2; 1.657 mg H_2O.
Found %: C 61.73; H 4.95.
$C_{15}H_{14}SO_4$. Calculated %: C 62.06; H 4.82.

5. Synthesis of 4-Hydroxy-4-chlorodiphenyl Sulfone

We took 19.2 g (0.1 mole) of p-chlorobenzenesulfonic acid and 18.8 g (0.2 mole) of phenol.

Heating lasted 12 hours at 240-245°. After the reaction was complete, the excess phenol was driven off with steam. After filtration, the residue in the distilling flask yielded a precipitate that was dissolved in 100 ml of ethyl alcohol, treated with a small amount of activated charcoal, and quickly filtered. A product in the form of white lamellae was obtained from the alcoholic solution after it had been reduced by evaporation to 2/3 of its initial volume and then cooled. M.p. 155-156°. Yield: 4 g (15% of theory). The substance contains sulfur and chlorine. It is readily soluble in ethyl alcohol, methanol, and alkalies; it dissolves with difficulty in benzene, ether, toluene, nitrobenzene, pyridine, and organic and mineral acids.

3.833 mg substance: 7.58 mg CO_2; 1.168 mg H_2O.
Found %: C 53.90; H 3.41.
$C_{12}H_9SO_3Cl$. Calculated %: C 53.64; H 3.35.

3.312 mg substance: 1.722 mg AgCl .
Found %: Cl 12.85.
$C_{12}H_9SO_3Cl$. Calculated %: Cl 13.06.

6. Synthesis of 4-Hydroxy-5-methyl-4'-chlorodiphenyl Sulfone

We used 21.6 g (0.2 mole) of o-cresol and 19.2 g (0.1 mole) of p-chlorobenzene sulfonic acid.

Heating lasted 12 hours at 240-245°. After the reaction was complete, a product in the form of thin prismatic needles with a m.p. of 229-230° was isolated from the reaction mass by treatment similar to that described above (Experiment 5). Yield: 9.3 g (33% of theory). It is readily soluble in methanol, ethyl alcohol, and caustic alkalies, but dissolves with difficulty in nitrobenzene and pyridine. It is hardly soluble in benzene, toluene, and ether. It is soluble in acetic and sulfuric acids upon heating. It reacts with $FeCl_3$ to color the solution red. It combines with diazo or para nitroaniline to yield a red dyestuff.

3.490 mg substance: 7.121 mg CO_2; 1.273 mg H_2O.
Found %: C 55.64; H 4.08.
$C_{13}H_{11}SO_3Cl$. Calculated %: C 55.31; H 3.90.

3.542 mg substance: 1.796 mg AgCl.
Found %: Cl 12.36.
$C_{13}H_{11}SO_3Cl$. Calculated %: Cl 12.58.

0.0416 g substance: 0.0359 g $BaSO_4$.
Found %: S 11.60.
$C_{13}H_{11}SO_3Cl$. Calculated %: S 11.34.

Nitro derivative. Crystals, m.p. 157-158°. Synthesized by treating 2.82 g of 4-hydroxy-5-methyl-4'-chlordiphenyl sulfone dissolved in 15 ml of glacial acetic acid with 1.8 g of HNO_3 (sp. gr. 1.44) in the cold. Yield: 2.78 g (85% of theory).

3.709 mg substance: 0.148 ml N_2 (16°, 749.5 mm).
Found %: N 4.65.
$C_{13}H_{10}SO_5NCl$. Calculated %: N 4.53.

II. Nitrosation of Hydroxy Sulfones.

1. Nitrosation of 4-Hydroxy-5-methyl Diphenyl Sulfone

2.48 g (0.01 mole) of 4-hydroxy-5-methyl diphenyl sulfone is dissolved in 25 ml of 0.5N NaOH, and 0.72 g of 100% nitrite is added, after which the solution is chilled to 0°, by adding ice. 1N H_2SO_4 is added drop by drop, with vigorous stirring, to the chilled solution until its reaction is slightly acid. Toward the end of the reaction, the reaction mass exhibits an acid reaction with Congo paper and exhibits a reaction with iodized starch paper. After nitrosation is complete, a precipitate was isolated from the reaction mass; it fused at 229-230° after recrystallization from alcohol. The substance contains no nitrogen. A mixed test sample of the initial product and the synthesized one exhibited no depression of the melting point.

2. Nitrosation of 4,4'-Dihydroxy Diphenyl Sulfone

A mixture, consisting of 2.5 g (0.01 mole) of 4,4'-dihydroxy diphenyl sulfone dissolved in 20 ml of 1N NaOH and 0.7 g of 100% nitrite, was chilled with ice to 0°. A solution of 1N H_2SO_4 was gradually added to the foregoing mixture of reagents, with constant stirring and the temperature kept from rising above 0°. In this case as well, the unchanged initial product was recovered after the reaction was complete. The nitrosation of 4,4'-dihydroxy diphenyl sulfone with a fourfold excess of nitrite under the conditions described above results in the formation of a product with a m.p. of 232-233°. Nitrosation with strong H_2SO_4 yielded a similar result. The substance contains nitrogen. It is soluble in glacial acetic acid, but hardly soluble in alcohols, toluene, benzene and ether. It dissolves in alkalies, turning the solutions yellow.

5.207 mg substance: 0.368 ml N_2 (20°, 478 mm).
Found %: N 8.10.
$C_{12}H_8N_2SO_8$. Calculated %: N 8.23.

To judge by the analytical results, what we synthesized was a dinitro derivative of 4,4'-dihydroxy diphenyl sulfone, instead of the expected nitroso compound.

SUMMARY

1. The feasibility of forming hydroxy sulfones from aromatic sulfo acids and phenols, with yields as high as 45% of theory, has been shown.

2. The action of nitric acid upon hydroxy sulfones, whether in molar proportions or in excess of the acid, results in the formation of nitro compounds instead of the expected nitroso compounds.

3. The syntheses of 4-hydroxy diphenyl, 2-hydroxy-5-methyl diphenyl, 4-hydroxy-5methyl diphenyl, 4-hydroxy-6-methyl diphenyl, 4-hydroxy-4'-chlorodiphenyl, and 4-hydroxy-5-methyl-4'-chlorodiphenyl sulfones, and of their nitro, bromo, methoxy, and acetoxy derivatives, are described.

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SULFONATION AND SULFO ACIDS OF ACIDOPHORIC COMPOUNDS

VIII. INVESTIGATION OF SULFONATING AGENTS

A. P. Terentyev, L. A. Kazitsyn and S. E. Suvorova

Organic Chemistry Laboratory of Moscow State University

Numerous successful efforts to sulfonate acidophic compounds by the method developed by us [1] led us to gather all the preliminary data on the sulfonation of these substances by other sulfonating agents and to examine in detail the feasibility of replacing the latter by pyridine sulfotrioxide. The sulfonating agents we chose were sulfuric acid and sulfur trioxide, without a solvent as well as in such solvents as benzene, dichloroethane, ether, acetic anhydride, dimethylaniline, pyridine, and the addition products of sulfuric anhydride and dimethylaniline, dioxane, and trimethylamine. We chose furan and sylvan as typical sulfonation objects.

Sulfuric Acid

As we know, the direct action of concentrated sulfuric acid upon furan compounds results in their profound modification. The reaction is usually accompanied by the evolution of considerable heat, blackening, and evolution of sulfur dioxide. But we know from the work done by V. Meyer [2] that he was able to hit upon conditions for the sulfonation of thiophene, employing high dilution in an inert solvent. But this method cannot be used with thiotolene and other homologues of thiophene: they are more sensitive to acids than thiophene itself [3].

We resolved to test the action of sulfuric acid on furan and sylvan in benzene, dichloroethane, acetic anhydride, dimethylaniline, and pyridine. In benzene and dichloroethane, as well as in ether and acetic anhydride (which we chose by analogy with the nitration reaction [4]), sylvan and furan underwent profound resinification when acted upon by sulfuric acid. We were unable to discover even traces of sulfo acids. At molecular ratios that do not exceed 1:1, sulfuric acid did not react with furan or sylvan in pyridine and dimethylaniline, even when the mixture was heated to 120°. When the sulfuric acid was used in excess, we noticed resinification, and the filtrate contained no barium ions after the usual treatment with barium carbonate.

Sulfur Trioxide

The action of sulfur trioxide in dichloroethane resulted in the resinification of furan and sylvan. Sulfur trioxide also resinified furan and sylvan in acetic anhydride, even when used in great excess. But in this case we were able to detect traces of sylvansulfonic acid.

In pyridine, sulfur trioxide possesses sulfonating effect on acidophobic compounds only when the sulfur trioxide and pyridine are used in equimolecular proportions. When there is an appreciable deficiency of pyridine, the acidophobic substance is naturally resinified.

When we tried to effect sulfonation in a pyridine medium, pyridine sulfotrioxide did not react with the substance to be sulfonated even when heated to 150°. In general, we noticed that even a slight excess of pyridine above the equimolecular quantity slows down the sulfonation reaction greatly. For such compounds as the dienes, in particular, the pyridine sulfotrioxide should not contain even a trace of pyridine. In this case, the presence of a almost infinitesimal quantity of pyridine made it necessary to prolong the sulfonation time considerably and to raise the temperature required for the normal reaction. Some impurities – especially sulfur dioxide – affect the sulfonating action of pyridine sulfotrioxide considerably. We synthesized pyridine sulfotrioxide from sulfur trioxide driven off from commercial oleum, which contained sulfurous acid, of course. We absorbed the mixture of sulfur trioxide and dioxide in dichloroethane, and added pyridine to the solution. The pyridine sulfotrioxide thus produced proved to be useless. It did not sulfonate even so reactive a substance as sylvan. We therefore henceforth always carried out the reaction with solid sulfur trioxide, prepared by distilling it from oleum with a desorber. No redistillation of the sulfur trioxide was required.*

Coordination Compounds of Sulfur Trioxide

Compounds of the R_3NSO_3 type include, in addition to pyridine sulfotrioxide, which we have studied in detail, compounds of sulfur trioxide with dimethylaniline [5], trimethylamine [6], and with their oxygen analogue: dioxane sulfotrioxide.

It is known from the literature that dimethylaniline sulfotrioxide is an extremely unstable compound, which readily transforms into p-dimethylanilinesulfonic acid [7]. We were never able to synthesize dimethylaniline sulfotrioxide – it rearranges readily into the corresponding acid. We did not investigate the causes of our failures, since it was quite obvious that a substance so freakish in synthesis and so unstable could not replace pyridine sulfotrioxide.

Trimethylamine sulfotrioxide was synthesized by the direct action of sulfur trioxide upon trimethylamine. It is stable: it can be recrystallized from hot water and undergoes no change upon prolonged storage. Sulfonation tests with this reagent indicated that it yields up its sulfur trioxide with great difficulty. It sulfonates furan when heated in sealed tubes for 20 hours at 100°, with a yield of 15.5% of furansulfonic acid.

Dioxane sulfotrioxide was first synthesized in 1938 by Suter [8]. He synthesized it by letting sulfur trioxide act upon dioxane at 0°. Dioxane sulfotrioxide is an unstable substance, disintegrating fairly rapidly at room temperature by opening its ring; it cannot be kept for any length of time. It would seem that its sulfonating action ought to be extremely close to that of pyridine sulfotrioxide. In fact, Suter used it widely to sulfonate unsaturated compounds, [8]. In view of the instability of this addition compound, he always used it freshly prepared. We synthesized dioxane sulfotrioxide by Suter's method and used it to sulfonate furan. When dioxane sulfotrioxide is reacted with furan in a dichloroethane solution at room temperature, considerable heat is evolved and resinification occurs. The reaction mass grows darker even at 0°. The next day the reaction products were treated with a paste of barium carbonate, and the

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* Very frequently we have noticed that in some cases carefully prepared sulfotrioxide possesses worse sulfonating properties than that containing a slight trace of sulfur trioxide.

filtrate was evaporated. The substance isolated proved to be a mixture of barium salts of the sulfo acid, produced by opening the dioxane and furan rings.

Evaluation of Results

There is reason to believe that a reagent can be used to sulfonate acidophobic compounds if two basic conditions are fulfilled:

1) The reagent must yield up its sulfur trioxide fairly easily.

2) The coordination compound constituent that reacts with the sulfur trioxide must be a strong enough base to form a salt of the synthesized sulfo acid. The reagent must be fairly stable under normal conditions and must be able to be stored for a long time, for purely practical reasons of preparation.

When sulfur acid and sulfur trioxide are employed, either by themselves or in solvents, the neutralization conditions for the synthesized sulfo acids are not satisfied. On the other hand, sulfates of tertiary amines retain sulfuric acid too strongly, and the sulfonation reaction does not occur at all.

In comparing the sulfonating action of the addition product of sulfur trioxide and dioxane, pyridine, dimethylaniline, and trimethylamine, we can note the differing degree in which the foregoing conditions are fulfilled. The sulfonating action of these products may possibly be directly related to the basicity of the coordination-complex constituent.

Base	K
Dimethylpyrone	$2 \cdot 10^{-11}$
Dimethylaniline	$2.4 \cdot 10^{-9}$
Pyridine	$2.04 \cdot 10^{-9}$
Trimethylamine	$5.55 \cdot 10^{-4}$

Unfortunately, there are no data for dioxane. We assume, on the basis of the foregoing table of dissociation constants, that the sulfonating action of dimethylaniline sulfotrioxide ought to be like that of pyridine sulfotrioxide. This may be so, but the ease with which the benzene ring itself can be sulfonated prevents the practical employment of dimethylaniline sulfotrioxide as a sulfonating agent.

Trimethylamine is a strong base, as the table indicates, and yields up its sulfur trioxide very reluctantly. Dioxane sulfotrioxide yields its sulfur trioxide readily, but it obviously does not neutralize the synthesized sulfo acids of the furan compounds adequately.

In conclusion, we may state that pyridine sulfotrioxide possesses the optimum combination of relative ease with which the sulfur trioxide is given up and neutralization of the synthesized sulfo acid. Moreover, an outstanding advantage of pyridine sulfotrioxide is its comparative stability: it may be kept at room temperature for several days, even exposed to the air; it reacts very slowly with cold water; and it is stable when heated to 200°. In hermetically sealed containers it can be kept for a long time (3 to 4 years).

The substances sulfonated by pyridine sulfotrioxide and the methods by which this reaction is effected were the subject of previous reports from our laboratory [1], and we therefore shall not repeat this aspect of our research here.

The closest homologue of pyridine – picoline – combines with sulfur trioxide, forming a similar compound. We synthesized picoline sulfotrioxide and employed it to sulfonate vinyl ethers. The yields were the same as those obtained in sulfonations with pyridine sulfotrioxide.

SUMMARY

Various sulfonating agents have been considered. Tests were made with furan, sylvan, and some other acidophobic compounds.

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* See CB translation pp. 481, 487, 763. (other translations not yet paginated).

SYNTHESIS AND POLYMERIZATION OF UNSATURATED ORGANIC SILICON COMPOUNDS

I. SYNTHESIS OF DIALLYLDIETHYLSILANE

B. I. Yakovlev

Much new research has been published during recent years in the field of organic silicon compounds, which are of great scientific and practical interest. The polymerization of unsaturated compounds is a new line of attack in the synthesis of organic silicon compounds of high molecular weight. This line of attack is particularly inviting, since it affords the possibility of synthesizing new organic silicon polymers with high dielectric properties and improved refractive properties.

There are a few publications in the literature on the synthesis of unsaturated organic silicon compounds containing brief references to the capacity of this type of compound to undergo polymerization at high temperature.

Ushakov and Itenberg [1] synthesized vinyltriethylsilane, but they did not find it had any tendency to polymerize when heated. Volnov and Reutt [2] observed that phenylethynylethoxysilanes polymerized during their synthesis. Hurd [3] synthesized vinyltrichlorosilane, divinyldichlorosilane, vinylmethyldichlorosilane, allyldichlorosilane, allyltrichlorosilane, allylmethyldichlorosilane, allyldimethylchlorosilane, and diallyldichlorosilane. The synthesis of tetra-allylsilane is described in Kropa's patent [4].

That is why the synthesis of allyl, vinyl, and ethynyl derivatives of silicon, the study of their ability to be polymerized, and investigation of the properties of the polymers synthesized, were of considerable interest.

We ran a series of experiments to synthesize diallyldiethylsilane $(C_3H_5)_2Si(C_2H_5)_2$, not described hitherto in the literature, with a view to ascertaining its polymerizability. Diallyldiethylsilane was synthesized by the action of diethyldichlorosilane upon allylmagnesium bromide in an ether solution

$$2(CH_2{=}CH{-}CH_2)MgBr + (C_2H_5)_2SiCl_2 \longrightarrow$$

$$\longrightarrow (CH_2{=}CH{-}CH_2)_2Si(C_2H_5)_2 + MgCl_2 + MgBr_2.$$

Yield (in terms of diethyldichlorosilane) was 55 to 60%.

EXPERIMENTAL

A mixture of 37 g of allyl bromide and 100 ml of ether was gradually added to 6.1 g of magnesium chips in a round-bottomed flask fitted with a stirrer, a mercury seal, and a reflux condenser. Then 10 g of diethylsilane dichloride (b.p. 128.5-130°) was gradually added to the allyl magnesium bromide thus produced. The mixture was then heated for 5 hours, and after it had cooled,

it was decomposed by a 25% solution of NH_4Cl with ice. The ether layer was removed and desiccated, and the residue distilled in vacuum with a column. This yielded 5.5 g of a substance with a b.p. of 91-92° at 34 mm.

The synthesized substance was carefully analyzed to determine its double bonds and its silicon content. Determination of its double bonds was effected by titration with a solution of bromine in carbon tetrachloride and with a Kaufman solution. The determinations made by these two methods yielded results that agreed closely. The silicon was determined by burning a weighed batch of the substance (0.2-0.3 g) with a mixture of concentrated H_2SO_4 and HNO_3, with subsequent determination of the SiO_2.

The constants of diallyldiethylsilane are as follows:

B.p. 91-92° at 34 mm; d_4^{20} 0.8076; n_D^{20} 1.4594.

Its molecular weight was determined cryoscopically in benzene:

0.1218 g substance: 14.10 g benzene: Δt 0.26°

Found: M 169.4
$C_{10}H_{20}Si$. Calculated: M 168.06

0.1246 g substance: 0.0438 g SiO_2.
Found %: Si 16.42.
$C_{10}H_{20}Si$. Calculated %: Si 16.66.

The bromine number of diallyldiethylsilane was found to be 193.3 (computed value: 189.8). Diallyldiethylsilane can be polymerized in the presence of benzoyl peroxide and other catalysts.

The author expresses his thanks to Prof. M.M.Koton for his guidance in this research and for useful advice.

SUMMARY

Diallyldiethylsilane was synthesized by the reaction of allylmagnesium bromide with diethyldichlorosilane, and its constants were described.

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THE ALKALOIDS OF LEONTICE EWERSMANNI BGE AND LEONTICE ALBERTI BGE

S. Yunusov and L. G. Sorokina*

Alkaloid Chemistry Laboratory of the Institute of Chemistry of the USSR Academy of Sciences

Very little chemical research has been done on the plants of the genus Leontice (family Bereberidaceae). The only data in the literature deal with Leontice thalictrum (Caulophyllum thalictroides Mich) [1] and Leontice Ewersmanni Bge [2]. Lloyd isolated an amorphous alkaloid from the former plant, which he called "caulophylline." Power and Solway isolated this substance in pure crystalline form and established its identity with methylcytisine [1]. In 1932, Orekhov and Konovalova [2] isolated a total of 0.4% of alkaloids from the tubers of the Central Asian species Leontice Ewersmanni Bge (period of vegetation not indicated), and, when they analyzed this complex mixture of alkaloids, they succeeded in isolating three alkaloids; one of them, named "leontamine," was described in detail, with its composition given as $C_{14}H_{26}N_2$. Leontamine forms a crystalline hydrochloride (melting point not given), a picrate with a m.p. of 194-195°, and a diiodomethylate with a m.p. of 265-268° (with decomposition). The second alkaloid was obtained as a picrate (m.p. about 250°) from which a crystalline base with a m.p. of 116-118°, which they called "leontidine," was isolated. This alkaloid forms a crystalline hydrochloride with a decomposition temp. of 293°. The authors were unable to establish the composition formula of this base because of the small quantity available to them. The picrate of the third alkaloid, with a m.p. of 178-190°, was isolated from the mother liquor after the leontidine had been eliminated. They were unable to form a base from this picrate.

We tested the above-ground and underground parts of Leontice Ewersmanni Bge and its seeds during various vegetation periods, but Leontice Alberti Bge was tested during only one period of vegetation. We collected large quantities of tubers and above-ground portions of L.Ewersmanni Bge at almost the very end of the flowering period, when fruit began to form (April 20, 1945, in the Kelesk district near Tashkent). Extraction of the above-ground parts of L. Ewersmanni Bge with dichloroethane yielded a mixture of alkaloids totaling 0.87% of the weight of the air-dried plant. The alkaloids constituted a thick oil, from which a crystalline hydrochloride totaling 50% by weight of the alkaloid total weight (acid mother liquor "A") was readily obtained in an acetone solution by adding alcoholic hydrochloric acid. A crystalline base was isolated from this hydrochloride after recrystallization from alcohol; it had a m.p. of 119-120°, $(\alpha)_D$ 188.7° after recrystallization from petroleum ether. The picrate synthesized from this base carbonized at 250°. An iodomethylate was synthesized with a m.p. of 275°. Though all these physical constants of the base and its salts differ from those of the above-mentioned leontidine, we take it that this alkaloid is identical with leontidine, and we decided to retain that name as given to it by the authors; the discrepancies in the constants is most probably

*Deceased

due to the fact that the authors did not isolate leontidine in a pure enough state.

The data of elementary analysis, molecular-weight determination, and determination of chlorine in the hydrochloride and of iodine in the iodomethylate enabled us to establish the composition formula of leontidine as $C_{15}H_{20}N_2O$. Leontidine is a monoacid tertiary base that forms a monohydrochloride and a monoiodomethylate; the second nitrogen atom and the oxygen atom are in an unreactive form; this speaks in favor of the presence of a $>N-CO-$ group. Leontidine is stable toward bases; when boiled with a strong alcoholic base, the initial base was recovered. Leontidine instantaneously decolors permanganate in a sulfuric-acid solution, but leontidine was again recovered in catalytic hydrogenation (by the Adams method) and in reduction (by the Ladenburg method).

The base is recovered from the acid mother liquor "A"; the base was divided into two fractions according to boiling points in vacuum. A liquid alkaloid (1.7% of the total) isolated from the first fraction yielded a satisfactorily crystallizing picrate with a m.p. of 204-205° and caused no depression when mixed with a picrate prepared from pure pachycarpine. A third alkaloid was isolated from the second fraction as a hydroiodide. The base obtained from the hydroiodide (about 5% of the total) is a transparent oil, which yields a readily crystallizable perchlorate, hydroiodide, and iodomethylate. The melting points of the salts and of the iodomethylate, as well as the rotation of this alkaloid, are very close to those of d-lupanine, which suggests their identity.

Name of derivative	Isolated alkaloid	d-Lupanine
Hydroiodide	186-187°	190°
Perchlorate	204-205	210
Iodomethylate	238-239	239
Rotation of hydroiodide . .	$[\alpha]_D$ + 44.4	$[\alpha]_D$ + 44

We were unable to identify them conclusively because we had no d-lupanine available to us.

From the second fraction of the mother liquor we also obtained d-lupanine perchlorate, with a m.p. of 232°, (with decomposition), from which, in turn, we isolated a fourth crystalline alkaloid with a m.p. of 103-104°, $[\alpha]_D$ 0°, with a composition of $C_{15}H_{24}N_2O$. The yield was 10%. This alkaloid proved to be different from those hitherto known, and we therefore named it "leontine." Leontine, like leontidine, forms mono salts and a monoiodomethylate, i.e., the second nitrogen atom and the oxygen are inactive, and the substance behaves like a saturated compound. Comparison of the formulas of leontidine, $C_{15}H_{20}N_2O$, and leontine, $C_{15}H_{24}N_2O$, indicates that leontine is tetrahydroleontidine.

The tubers of L.Eversmanni Bge gathered at the same time as the above-ground portions of the plant – at the end of the flowering period – yielded 0.17% of a mixture of alkaloids; separation treatment like that described above yielded 50% (of the total alkaloids) of leontidine, about 15% of leontine, and 5% of a colorless, mobile, oily base that boiled at about 200° at 7 mm.

The latter base yields a crystalline mixture of the mono- and dihydrochlorides with a m.p. of 267-268° with decomposition. All these data clearly indicate that this base is doubtless identical with leontamine. Owing to the small quantity of leontamine at our disposal, we were unable to recover it from the purified salts of this base, and that is why we could not determine the composition formula of this alkaloid. But we assume that leontamine has the composition of $C_{15}H_{26}N_2$, and not that of $C_{14}H_{28}N_2$, and apparently is a stereoisomer (an

optical antipode) of pachycarpine. In general, it is probable that the pachycarpine skeleton structure underlies the structures of both leontine and leontidine; these alkaloids differ from each other in the position of the carbonyl group and of the double bond, and in their spatial configuration.

Again we gathered a large quantity of seeds, tubers, and above-ground parts of L.Ewersmanni Bge at one time in the district mentioned above, doing this during the repening season, when the seeds are not yet fully ripe, and the above-ground parts of the plant were still green, but the lower leaves were dry and contained almost no more alkaloid. 1.1% of alkaloids was isolated from the coarse-ground seeds (each seed was split into 4 or 5 pieces). Separation of this alkaloid mixture by the method described above enabled us to isolate 60% of leontidine and 10% of leontine. Because of its small volume, the mother liquor was not investigated for the time being. The percentage of alkaloids in the leaves and stems was only half as great, totaling 0.44% of the total weight. The alkaloid percentage in the tubers was twice as high, the yield of the mixed bases being as much as 0.32%. There was not much change in the composition and quantitative proportions of the alkaloids.

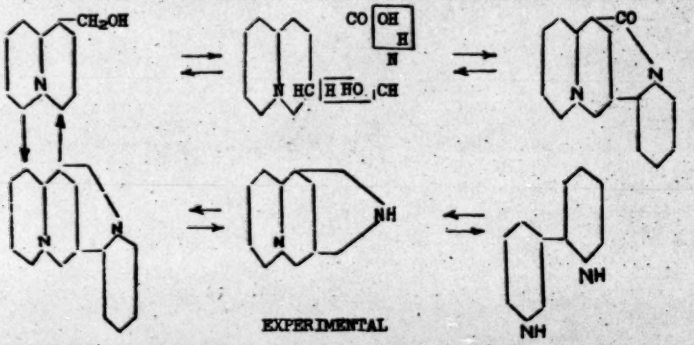
Traces of the alkaloids were found in the leaves and stems after the above-ground portions of the plant had died away, whereas the percentage of alkaloids in the seeds rose to 1.4% and in the tubers to 0.6%. In this period as well, the principal plant alkaloids continued to be leontidine and leontine. Thus, the fact that they isolated a total of 0.4% of alkaloids justifies our assumption that Orekhov and Konovalova did their research on the tubers of this plant during the period when the seeds were ripening.

We investigated individual parts of the plant at other seasons of the year and learned that the above-ground portion of the plant contains a maximum of alkaloids during the period of intensive growth, there being less alkaloid in the tubers at this time. The percentage of alkaloids in the above-ground plant begins to drop in the leaves and stems that were the first to appear and reach their maximum growth. After the above-ground plant has died away there is practically no alkaloid left in the dry stubble. It is during this period that the seeds and tubers contain the maximum amount of alkaloids.

We assume that, together with other substances, the alkaloids are regulators of plant development. We turned the leontidine alkaloid over to the Chair of Plant Physiology of the Tashkent Agricultural Institute for research. It was found that wetting the seeds with a dilute solution of this alkaloid greatly accelerates the germination of the seed, according to the findings of Yenileyev, and increases the germination of seeds of different varieties of cotton.

Leontice Alberti Bge is a small, uncommon, mountain plant. We collected its above-ground and underground portions simultaneously at the beginning of the flowering season (June 5, 1945) in the Angrensk district of Tashkent Region, at the upper end of the Lyashkarak valley. The total alkaloids were isolated by extraction with dichloroethane. The tubers yielded 0.75% of an alkaloid mixture. The latter was separated into two fractions according to solubilities in ether and chloroform; the same crystalline hydrochloride was obtained from an acetone solution of each fraction: this crystalline hydrochloride yielded a crystalline base that proved to be identical with methylcytisine. The latter constituted about 60% of the total alkaloids. After recovery of the mixture of bases, a liquid base was isolated by distillation in vacuum of the mother liquors, but it was investigated no further because of the small quantity available. The above-ground portion of Leontice Alberti Bge yielded 1% of a mixture of bases, which was extracted from an alkaline solution by ether and chloroform. The bases obtained from the ether extract were separated into two fractions by vacuum

distillation. Methylcytisine partially crystallized out of the first fraction upon standing, the second fraction consisting largely of methylcytisine. We were able to isolate a small amount of a crystalline alkaloid with a m.p. of 180-183° from a chloroform extract. Thus, methylcytisine constitutes 37% of the total alkaloids isolated from the above-ground portions of L. Alberti Bge during this period of development. The crystalline and liquid alkaloids isolated from the mother liquors after the methylcytisine had been removed apparently belong to a related series of alkaloids: cytisine, panhycarpine, lupinine, anabasine, etc., which may be formed within a plant from a single substance. That is why they are often found together and are converted from one to another during the plant's period of vegetation.



EXPERIMENTAL

I. Isolation of Alkaloids from Leontice Ewersmanni Bge

1. 7.5 kg of the above-ground portions of the plant was ground up and wetted with 5% ammonia, after which it was exhaustively extracted with dichloroethane. The dichlorcethane extract was leached out with 10% H_2SO_4. The filtered acid solution was chilled and then alkalinized with 25% ammonia, the base that separated out being extracted with dichloroethane; the dichloroethane was driven off after the mixture had been desiccated with anhydrous potash. The yield was 66 g (0.87%). The mixture of alkaloids thus produced was dissolved in 200 ml of acetone, and an alcoholic solution of HCl was added a drop at a time to the solution until its reaction was faintly acid. This caused a pale-yellow precipitate of crystalline leontidine hydrochloride (32 g) to settle out (acid mother liquor "A":

0.1768 g substance in 15 ml methanol: $\alpha - 0.8°$; $\underline{1}$ 1 dm; $[\alpha]_D - 67.8°$.

0.1388 g substance: 4.92 ml 0.1N $AgNO_3$.
0.1088 g substance: 3.83 ml 0.1N $AgNO_3$.
Found %: Cl 12.4, 12.3.
$C_{15}H_{20}ON_2 \cdot HCl$. Calculated %: Cl 12.5.

Leontidine. 25 g of the purified leontidine hydrochloride was dissolved in water, and an excess of a saturated solution of NaOH was added. The base was then completely extracted from the alkaline solution with benzene. After drying with potash and driving off the benzene, we had left 22 g of a light oil, which crystallized completely upon standing. It had a m.p. of 119-120° after recrystallization from petroleum ether. Leontidine is readily soluble in water, ether,

benzene, alcohol, and acetone, but only poorly soluble in petroleum ether.

0.1584 g substance in 13 ml methanol; α – 2.3°; $\frac{1}{2}$ 1 dm; $(\alpha)_D$ –188.7°.

0.1188 g substance: 0.3196 g CO_2; 0.0866 g H_2O.
0.1164 g substance: 0.3150 g CO_2; 0.0830 g H_2O.
3.3500 ml substance: 0.3500 ml N_2 (20°, 718 mm).
4.45 mg substance: 0.4700 ml N_2 (20°, 726 mm).
Found %: C 73.37, 73.8; H 8.15, 7.98.
N 11.1, 11.35.
$C_{15}H_{20}ON_2$. Calculated %: C 73.7; H 8.49; N 11.4.

0.1804 g substance: 7.39 ml 0.1N HCl (methyl red).
0.1516 g substance: 6.23 ml 0.1N HCl (methyl red).
Found: M 244.1, 243.3.
$C_{15}H_{20}ON_2$. Calculated: M 244.

Picrate. Leontidine was dissolved in alcohol and mixed with an alcoholic solution of picric acid. This caused the crystalline picrate to precipitate out; it was recrystallized from water and carbonized at 250°.

Iodomethylate. 1 g of leontidine was dissolved in 10 ml of methanol, 4 ml of methyl iodide was added to the solution, and the whole was heated with a reflux condenser over a water bath for 6 hours. After the solution had cooled, acicular crystals (1.2 g) precipitated out. After recrystallization from alcohol they fused at 274-275° with decomposition.

0.1351 g substance: 3.48 ml 0.1N $AgNO_3$.
0.1134 g substance: 2.97 ml 0.1N $AgNO_3$.
Found %: I 32.7, 33.2.
$C_{15}H_{20}ON_2 \cdot CH_3I$. Calculated %: I 32.9.

After the acetone had been evaporated from mother liquor "A" there remained 34 g of a mixture of alkaloid hydrochlorides as a thick brown mass, which was dissolved in water, after which a saturated solution of NaOH was added. The base that separated out was fully extracted with ether. The ether solution was dried with potash, and the ether was driven off. The yield was 20 g of a light-yellow oil, which was then fractionated in vacuum:

Fraction I: 140-190° (7 mm) 1 g;
Fraction II: 190-205° (7 mm) 16 g.

Fraction I (1 g of a colorless, transparent oil) was dissolved in alcohol and an alcoholic solution of picric acid was added; this caused a crystalline precipitate to settle out. Recrystallization from alcohol yielded a picrate as yellow needles with a m.p. of 204-205°, which exhibits no depression when fused with a picrate prepared from pure pachycarpine.

Fraction II (16 g of a thick transparent oil) was dissolved in alcohol, and strong hydroiodic acid was added a drop at a time until the reaction was slightly acid; this caused crystalline lupanine hydroiodide (acid mother liquor "B") to precipitate out. M.p. of 186-187° after recrystallization from alcohol. The yield was 2.6 g.

0.072 g substance in 16 ml water; α + 0.2°; $\frac{1}{2}$ 1 dm; $(\alpha)_D$ +44.4°.

0.0840 g substance: 2.23 ml 0.1N $AgNO_3$.
0.0784 g substance: 2.08 ml 0.1N $AgNO_3$.
Found %: I 33.7, 33.69.
$C_{15}H_{24}ON_2HI$. Calculated %: I 33.77.

Lupanine was isolated by adding an alkali to an aqueous solution of the hydroiodide (2.5 g) and then extracting with ether. After the ether had been driven off, there remained 1.5 g of a light oil, from which the perchlorate was obtained by mixing a saturated aqueous solution of ammonium perchlorate with a solution of lupanine hydrochloride. Lupanine perchlorate recrystallized from water has a m.p. of 204-205°.

Lupanine iodomethylate was prepared by adding 1 ml of methyl iodide to a solution of 0.3 g of the base in 2 ml of acetone. The crystalline iodomethylate precipitated out upon cooling. M.p. 238-239°.

After the solvent had been evaporated, the base was recovered from acid liquor "B" by the addition of an alkali and extraction with dichloroethane. The solvent was driven off, and the residue distilled in vacuum at 195-205° (7 mm). The yield was 9 g; the end product crystallized upon standing. We prepared leontine perchlorate (7 g), which crystallized readily from water and had a m.p. of 230-232°.

Leontine was isolated by adding an alkali to an aqueous solution of the perchlorate and then extracting with ether. After the ether had been driven off, there remained an oil (6 g), which crystallized completely. It had a m.p. of 103-104° after recrystallization from petroleum ether. Leontine dissolves readily in water and in all the usual organic solvents, with the exception of petroleum ether.

0.1070 g substance in 15 ml methanol; α 0°.
0.1050 g substance: 0.2818 g CO_2; 0.0900 g H_2O.
4.70 mg substance: 0.470 ml N_2 (28°, 722 mm).
Found %: C 73.1; H 9.59; N 10.3.
$C_{15}H_{24}ON_2$. Calculated %: C 72.58; H 9.67; N 11.29.

0.1084 g substance: 4.45 ml 0.1N HCl.
Found: M 243.5
$C_{15}H_{24}ON_2$. Calculated: M 248.

Leontine iodomethylate was prepared by mixing an acetone solution of the base with methyl iodide. When the mixture was set aside to stand, a crystalline precipitate settled out. After recrystallization from a 1:1 mixture of alcohol and acetone, it had a m.p. of 290-292° with decomposition.

0.1062 g substance: 2.69 ml 0.1N $AgNO_3$.
Found %: I 32.16.
$C_{15}H_{24}ON_2 \cdot CH_3I$. Calculated %: I 32.56.

2. From tubers. 54 g (0.17%) of an alkaloid mixture was extracted by dichloroethane from 32 kg of L.Ewersmanni tubers ground to a coarse powder. From this mixture 31 g of crystalline leontidine hydrochloride was obtained in acetone solution. 20 g of the base was recovered from the acidified acetone solution by extraction with ether; this was fractionated in vacuum, yielding a 1st fraction: 134-140° (7 mm), 2.3 g (leontamine – a colorless, mobile oil); and a 2nd fraction: 190-210° (7 mm), 10 g of leontine.

Leontamine hydrochloride was prepared by adding an alcoholic solution of hydrogen chloride to the base, resulting in the formation of a crystalline mixture of leontamine mono- and dihydrochlorides with a m.p. of 192-196°.

Leontamine picrate was prepared by mixing alcoholic solutions of the hydrochloride of the base and of picric acid together. M.p. 195-196°.

Leontamine diiodomethylate, prepared in a solution of methanol, has a m.p.

of 267-268° with decomposition.

The 2nd fraction crystallized upon standing. The base was isolated (7 g), with a m.p. of 103-104° after recrystallization from petroleum ether; it exhibited no depression when mixed with leontine.

3. From seeds. A total of 66 g of alkaloids (1.1%) was isolated from 6 g of chopped seeds of L. Ewersmanni by extraction with dichloroethane. This was then dissolved in 400 ml of acetone, after which an alcoholic solution of hydrogen chloride was added, causing a crystalline deposit (39 g) to precipitate out. The base recovered from this hydrochloride has a m.p. of 119-120°. A test sample of the base, mixed with leontidine, caused no depression. After the leontidine hydrochloride had been eliminated, the base was recovered from the acidified mother liquor and distilled in vacuum (up to 210° at 9 mm). The yield was 10 g. The base crystallized upon standing. When recrystallized from petroleum ether it has a m.p. of 103-104° and causes no depression when mixed with leontine.

II. Isolation of Alkaloids from Leontice Alberti Bge

1. From tubers. 200 g of ground-up tubers of Leontice Alberti Bge was wetted with 5% ammonia and exhaustively extracted with dichloroethane. The dichloroethane extract was leached out with 10% H_2SO_4, and the acid solution alkalinized with NH_4OH and then extracted with dichloroethane until the dichloroethane exhibited no reaction for the alkaloid. The dichloroethane solution was desiccated, and then the solvent was driven off. This yielded 1.5 g of a dark oil (0.75% of the dry weight of the plant), which was dissolved in 5% H_2SO_4; the solution was alkalinized, and the alkaloids extracted, first with ether and then with chloroform. The ether extract yielded a light-yellow oil (0.8 g) after the solvent had been driven off. The base was dissolved in acetone; when an alcoholic solution of hydrogen chloride was added, a slightly yellow crystalline precipitate settled out (0.5 g). The hydrochloride recrystallized from alcohol has a m.p. of 250-256°.

The hydrochloride was dissolved in water, and 25% ammonia was added to the solution. The alkaline solution was extracted with chloroform. After the chloroform had been driven off, there remained a light-yellow oil, which crystallized (0.35 g). The base has a m.p. of 134-135° when recrystallized from benzine. It exhibits no depression when mixed with methylcytisine.

After the hydrochloride had been eliminated, the mother liquor was evaporated; the residue was dissolved in water, the solution alkalinized, and the alkaloid extracted with ether. The residue after the ether had been driven off was 0.4 g of a light-yellow oil, which was distilled in vacuum (8 mm); this yielded a highly mobile, almost colorless oil (0.2 g) which darkens on exposure to air. We were unable to prepare the crystalline picrate, hydrochloride, or hydroiodide.

0.5 g of the base obtained by driving off the chloroform was dissolved in acetone, and an alcoholic solution of HCl was added; this caused 0.5 g of a yellow crystalline precipitate to settle out. The base was recovered from this hydrochloride by adding ammonia to an aqueous solution of the hydrochloride and then extracting several times with chloroform. The 0.4 g of tar remaining behind after the chloroform had been driven off was dissolved in hot petroleum ether, from which white crystals, with a m.p. of 133-134°, settled out upon cooling. A sample caused no depression when mixed with methylcytisine.

2. From the above-ground portions. The alkaloids were extracted from 1.5 kg of the ground-up above-ground portions of L. Alberti Bge by the usual dichloroethane method. This yielded 15 g (1% of the dry weight of the plant) of a dark oil, which was dissolved in acid; the solution was alkalinized with ammonia and extracted, first with ether and then with chloroform. The ether solution was dried with potash and then distilled, yielding 10 g of a light-yellow oil, which was then redistilled in vacuum.

Fraction I: 110-160° (8 mm) 1 g – light-yellow, mobile oil.
Fraction II: 160-210° (8 mm) 6 g – thick yellow oil.
Undistilled residue. 3 g.

6 g of Fraction II was dissolved in 20 ml of acetone, and an alcoholic solution of hydrogen chloride was added to the solution. A white crystalline deposit precipitated out (5.1 g). The 5.1 g of the hydrochloride was dissolved in water, and a 25% solution of ammonia was added to the solution. The alkaline solution was extracted with chloroform. Driving off the chloroform yielded a crystalline residue (4.2 g), which was recrystallized from petroleum ether (m.p. 134-135°); it caused no depression when mixed with methylcytisine.

After the hydrochloride had been removed, the mother liquor was evaporated. The residue was dissolved in water, alkalinized, and extracted with ether. The residue after the ether had been driven off was 1.7 g of an oil; we were unable to break this oil down further.

The alkaloids of Fraction I crystallized in part. The crystals were separated out and recrystallized from petroleum ether (0.2 g; m.p. 134-135°); they caused no depression when mixed with methylcytisine. The residue after the crystals had been removed was 0.8 g of a mobile oil.

After the chloroform extract had been dried and the chloroform driven off, the residue left was 2.5 g of a dark tarry mass. The latter was dissolved in acetone, and an alcoholic solution of hydrogen chloride was added, causing a yellow tar to settle out. The acetone solution was decanted off, and 30 ml of alcohol was added to the residue.

The 0.5 g of white crystalline deposit that settled out was dissolved in water and alkalinized with ammonia; the resulting solution was extracted with chloroform. The dark tar (0.4 g) residue after the chloroform was driven off was dissolved, with heating, in gasoline (b.p. 80°); upon cooling slightly yellowish, silky crystals settled out. Their m.p. was 180-183° after triple recrystallization.

Picrate. The base was dissolved in alcohol, and a saturated alcoholic solution of picric acid was added to the solution. Fine acicular crystals settled out; they were recrystallized from alcohol and had a m.p. of 168-171° with decomposition.

After the hydrochloride had been removed, the mother liquor was evaporated. The residue was dissolved in water and extracted with ammonia, and the solution leached out with chloroform. A residue of 1.7 g of a dark-brown tar was left after the chloroform had been driven off; this tar was dissolved in gasoline with heating. Upon cooling, 1.2 g of crystals with a m.p. of 133-135° settled out of the gasoline; they were found to be identical with methylcytisine.

SUMMARY

1. The above-ground portions of Leontice Eversmanni Bge contain a maximum of alkaloids during the period of intensive growth; during this period the tubers contain a minimum quantity of the mixture of bases: Almost no alkaloids

remain in the dry stubble of the plant after the above-ground portions have died away. It is at this time that the ripe seeds and tubers contain a maximum quantity of the alkaloids.

2. 0.87% of an alkaloid mixture is isolated from the above-ground portions of Leontice Ewersmanni Bge gathered at the end of the flowering season. The mixture contains 50% leontidine, 10% leontine, 5% d-lupanine, and 1.7% pachycarpine.

0.17% of total alkaloids was isolated from the tubers that had been collected at the same time as the above-ground portions of the plant. This yielded 50% leontidine, 15% leontine, and 5% leontamine in pure state. During the ripening season, 1.1% of total alkaloids was isolated from the seeds, 0.44% from the leaves and stems, and 32% from the tubers.

3. Five alkaloids were isolated in pure state from the various organs of L. Ewersmanni Bge; one of them, a new alkaloid that we have named leontine, has the composition formula of $C_{15}H_{24}ON_2$. Another alkaloid, leontidine, was isolated in pure state and its formula established as $C_{15}H_{20}ON_2$. Leontidine is an unsaturated alkaloid, while leontine is saturated, but both of them are monoacid tertiary bases containing one atom of nitrogen and one atom of oxygen in an inactive form.

4. A total of 1% of alkaloids was obtained from the above-ground portions of Leontice Alberti Bge gathered at the beginning of the blossoming period. This total yielded methylcytisine (37%), an alkaloid with a m.p. of 180-183°, and a liquid base. The tuber of this plant contains 0.75% of a mixture of bases, 60% of which are methylcytisine and the liquid base.

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SYNTHESIS OF TETRAHYDROTUBANOL AND TETRAHYDROTUBAIC ACID

A. A. Shamshurin

Organic Chemistry Laboratory of the Samarkand Institute of Medicine

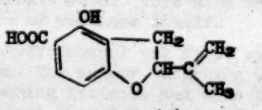
Tetrahydrotubaic acid (III) is the product of the complete hydrogenation of tubaic acid (I), as was discovered by Takei and associates [1] and Haller and La Forge [2]. As we know, tubaic acid, in turn, is the principal fragment of the rotenone molecule – the strongest of the modern insect and fish poisons of vegetable origin.

Tetrahydrotubanol is readily formed by the decarboxylation of tetrahydrotubaic acid.

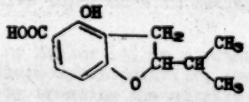
As an oxydihydrocarboxycoumaric acid with an isopropenyl side chain, tubaic acid undergoes singular conversions into various other acids during hydrogenation. Thus, energetic hydrogenation yields tetrahydrotubaic acid (III) together with the dihydrotubaic acid (II), these acids being formed by the opening of the furan ring at the oxygen atom and the former's loss of its asymmetrical center.

It is characteristic that when the hydrogenation is effected in an alkaline medium, isodihydrotubaic acid (IV) can be isolated from the reaction products. Isodihydrotubaic acid is an isomer of dihydrotubaic acid. In a neutral solution (IV) can be further hydrogenated to the tetrahydrotubaic acid.

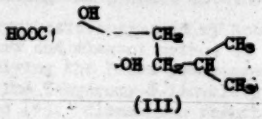
In the formation of isodihydrotubaic acid, the furan ring is opened without reduction of the double bond at the 2,3 position. This position of the double bond was considered probable by Takei [1].



(I)



(II)



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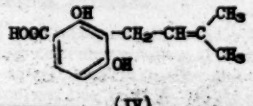
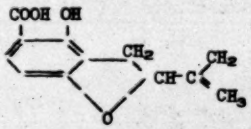


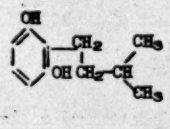
(IV)

All these reducing reactions of tubaic acid, with the formation of the corresponding intermediate products, are also characteristic of rotenone and its derivatives that contain the tubaic-acid group with the isopropenyldihydrofuran system.

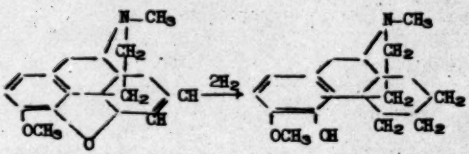
It should be further noted that the conversion of desoxycodeine (V) into tetrahydrodesoxycodeine (VI) by hydrogenation is similar to these hydrogenation processes with tubaic acid. The groups obtained resemble those present in tubaic acid, as is seen when the latter is written as (VII), and we bear in mind the $-O-\underset{|}{CH}-\underset{|}{C}-CH-$ group, comparable in its hydrogenation behavior to the conjugated system (Schopf's theory).



(VII)



(VIII)



(V) (VI)

Tetrahydrotubanol (VIII) played a part in the synthesis of tetrahydromethylderritol – a derivative of rotenone, synthesized under reducing conditions by the cleavage of rotenone with subsequent methylation. This synthesis was effected by Takei, Miyajima, and Ono [3] by condensing tetrahydrotubanol with homoasaronic acid. This also was of decisive importance in establishing the structure of rotenone itself.

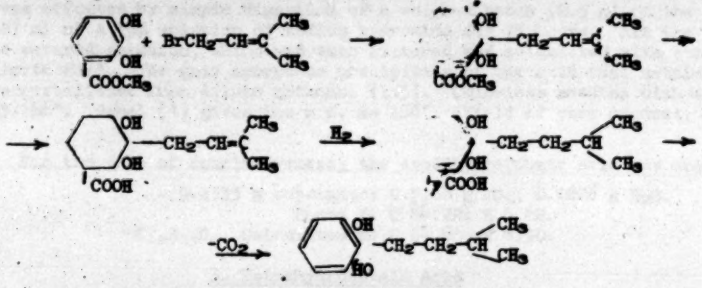
Tetrahydrotubanol was first synthesized by Haller [4] in a rather roundabout fashion. The author, starting with 2,6-dimethoxybenzonitrile, synthesized the corresponding ketimine and then the ketone by treating the nitrile with a Grignard reagent (iso-C_4H_9MgBr). He also succeeded in synthesizing 2-isoamylresorcinol (tetrahydrotubanol) by subjecting the ketone to a Clemmensen reduction and demethylating the product obtained with aluminum chloride.

The synthesis suggested by Robertson [5] was also complicated. He later proposed a new and elegant method of synthesizing tetrahydrotubanol with good yield by applying the Fries rearrangement to β-methylumbelliferone and then hydrolyzing the 7-hydroxy-8-isovaleryl-4-methylcoumarine to 2,6-dihydroxyisovalerophenone [6]. Clemmensen reduction of the latter yielded tetrahydrotubanol.

We describe below the synthesis of tetrahydrotubaic acid and tetrahydrotubanol by a direct method: the condensation of methyl β-resorcylate with isoprene hydrobromide under conditions that resemble the initial stage of the Späth synthesis of natural coumarin: osthol; the condensation of the monomethylate of

β-resorcyl aldehyde with the given bromide was employed in accordance with the author's instructions [7].

The equations involved in our synthesis are as follows:



The synthesized methylate of isodihydrotubaic acid was saponified to the free acid, and the latter was hydrogenated to tetrahydrotubaic acid.

The method of synthesizing isodihydrotubaic acid determines its structure unequivocally as that of an unsaturated acid with a double bond between the 2 and 3 carbon atoms. The course of the isoprene hydrobromide radical toward position 2 (between the hydroxyl groups) is typical; in the given case, we did not observe the formation of either open-chain isomers or traces of chromans, as could have been expected from the assumptions made by Claisen [8] and by other, more recent authors [9,10]. Decarboxylation of Compound (III) by the quinoline method with copper powder yielded tetrahydrotubanol. We tested the structure of the tetrahydrotubanol thus synthesized as follows: we condensed it with malic acid and methylated the synthesized 8-isoamyl-7-hydroxycoumarin with diazomethane, thus synthesizing dihydroosthol, exactly as in its synthesis by Haller and Acree [11].

EXPERIMENTAL

1.Methyl isodihydrotubanate

The initial methyl β-resorcylate had a m.p. of 118-119° (from dichloroethane).

24.6 g of the initial ester was dissolved in 75 ml of anhydrous benzene and, while the latter boiled, 2.3 g of metallic sodium was added in small portions. After 8 hours of heating with a reflux condenser, the reaction mixture took on a greenish-brown color; it was then cooled, 15 g of freshly prepared isoprene hydrobromide was added, and heating was continued for 6 more hours until the solution's reaction was neutral. Then the reaction mixture, from which a precipitate of sodium bromide settled out, was treated with ether and repeatedly washed with 5% sodium hydroxide. The extract was acidulated with dilute hydrochloric acid (1:3), exhaustively extracted with ether, and dried with sodium chloride. The dry residue after the solvent had been driven off was triple-recrystallized from aqueous methanol to which activated charcoal had been added. The yield was 6.20 g. M.p. 86-87°.

0.0992 g substance: 0.2461 g CO_2; 0.0590 g H_2O.
0.1244 g substance: 0.3875 g CO_2; 0.743 g H_2O.
Found %: C 67.67, 67.69; H 6.61, 6.64.
$C_{13}H_{16}O_4$. Calculated %: C 67.48; H 6.50.

2. Isodihydrotubaic Acid

The saponification of methyl isodihydrotubanate to free isodihydrotubaic acid was effected by simple digestion of a weighed batch (2.3 g) of the ester with 27 ml of a 15% solution of sodium hydroxide for 75 hours. All the substance entered solution, which was then filtered and acidulated with strong hydrochloric acid. The gray amorphous precipitate of the acid that settled out was recrystallized from dilute methanol (1:3). Colorless needles with a m.p. of 165-166°. Takei [1] gives the m.p. as 166°. Yield of pure product: about 2 g.

For the sake of conclusiveness, the isodihydrotubaic acid was analyzed.

0.1335 g substance: 0.3168 g CO_2; 0.0806 g H_2O.
Found %: C 64.72; H 6.62.
$C_{12}H_{14}O_4$. Calculated %: C 64.86; H 6.30.

3. Tetrahydrotubaic Acid

3 g of isodihydrotubaic acid, 0.5 g of fresh platinum oxide, and 150 ml of absolute alcohol were agitated together at room temperature in an atmosphere of hydrogen. The reaction mixture absorbed about 1 mole of hydrogen. After filtering, the alcohol was driven off at 30 mm, and the residue of tetrahydrotubaic acid was recrystallized twice from 25% alcohol. Colorless crystals; m.p. 206° (with decomposition). Yield: 2.2 g.

4. Tetrahydrotubanol

The tetrahydrotubaic acid (1.25 g) was decarboxylated by 6 g of copper powder in the presence of 50 ml of quinoline by heating the solution to boiling for one hour. After it had cooled, the mixture was diluted with ether and filtered; an ether extract was made of the filtrate and washed with 3% hydrochloric acid. The ether solution was desiccated with calcined sodium sulfate and evaporated. The residue was recrystallized from light gasoline (b.p. 60-80°). Colorless needles with a m.p. of 81.5-82.5°. According to the literature, the m.p. is 83-84°.

5. Dihydroosthol (8-Isoamyl-7-methoxycoumarin)

Dihydroosthol was synthesized, as stated in the general section of this paper, from the tetrahydrotubanol synthesized by us and malic acid, followed by methylating the intermediate 8-isoamyl-7-hydroxycoumarin with diazomethane, carefully complying with all the experimental conditions laid down by Haller and Acree. M.p. 83-84°. The above authors give the m.p. as 85°. Thus, the structure of the initial product as tetrahydrotubanol was convincingly proved by the synthesis of dihydroosthol.

SUMMARY

1. Isodihydrotubaic acid was synthesized by direct condensation of methyl β-resorcylate with isoprene hydrobromide in benzene in the presence of metallic sodium (Spath's reaction); the acid was hydrogenated in a neutral medium to tetrahydrotubaic acid.

Tetrahydrotubanol was synthesized by the decarboxylation of tetrahydrotubaic acid.

2. When treated with malic acid and after methylation of the intermediate product – 8-isoamyl-7-hydroxycoumarin, tetrahydrotubanol yields the already known compound, dihydroosthol.

3. The earlier conclusion regarding the presence of the double bond in isohydrotubaic acid was merely a preliminary one. This research conclusively proves the position of its double bond by the use of isoprene hydrobromide, a compound in which the position of this bond is known, in its synthesis.

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